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KINETIC STUDIES ON THE REACTIONS OF CHROMIUM(II) WITH NITRILE COMPLEXES OF PENTAAMMINECOBALT(III)

by

WILLIAM CLETUS HENRY KUPFERSCHMIDT

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
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To Jeanette

ABSTRACT

The reactions of chromium(II) with a series of nitrile complexes of pentaamminecobalt(III) have been studied. The complexes of acetonitrile, succinonitrile, cyanoacetamide and methylcyanoacetate are reduced by means of an outer-sphere mechanism. On the other hand, ligand transfer was shown to occur in the reduction of $(NH_3)_5CoNCCH_2CO_2^{2+}$ and a bridged-outer-sphere mechanism is thought to be operative. The results for the malononitrile complex are less definitive but are consistent with competing inner-sphere and bridged-outer-sphere reduction pathways.

The reaction of chromium(II) with $NCCH_2X$, X ≡ Cl, I proceeds by halogen abstraction to yield the radical $NCCH_2\cdot$, which is subsequently reduced by chromium(II) to yield $(H_2O)_5CrCH_2CN^{2+}$, IV-1. Analogous behaviour is observed for the $(NH_3)_5Co^{3+}$ complexes of $NCCH_2X$, X ≡ Cl, I where the novel complex $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, IV-2, is formed. Both IV-1 and IV-2 are reduced by chromium(II). The former is believed to undergo bridged-outer-sphere reduction by attack at the uncomplexed nitrile. The reactions of mercury(II) with both IV-1 and IV-2 were also studied. For the latter system, the product of reaction is $(NH_3)_5CoNCCH_2Hg(OH_2)^{4+}$.

Chromium(II) reduction of $(NH_3)_5CoNCCH{=}CHCN^{3+}$ proceeds by facile inner-sphere electron transfer to yield

$(H_2O)_5CrNCCH{=}CHCN^{3+}$, V-1. In the absence of chromium(II), V-1 aquates to $Cr(OH_2)_6^{3+}$ and free fumaronitrile. However, in the presence of chromium(II), both V-1 and free fumaronitrile readily undergo reduction to yield a variety of organochromium(III) products. Detailed kinetic and product studies were undertaken to determine the nature of these products and their mechanism of formation.

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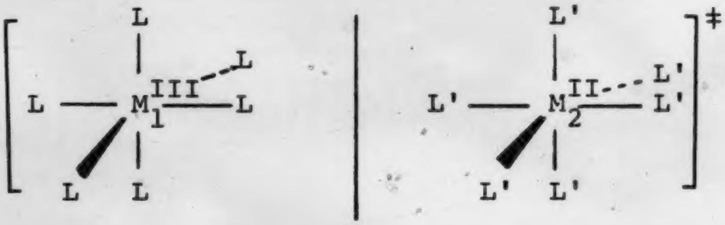
CHAPTER I

INTRODUCTION

The net result of an oxidation-reduction reaction between two metal ion complexes

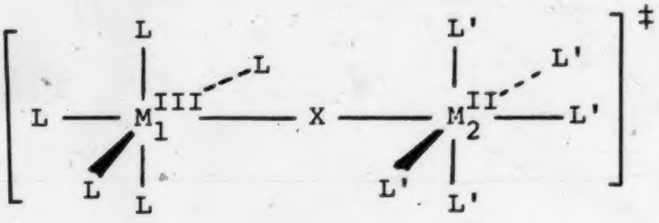
$$M_1^{III}L_n + M_2^{II}L'_n \longrightarrow M_1^{II}L_n + M_2^{III}L'_n \qquad (1.1)$$

is to transfer an electron from the reductant, $M_2^{II}L'_n$, to the oxidant, $M_1^{III}L_n$. Historically, such electron transfer reactions have been classified into two major categories, inner-sphere and outer-sphere.[1] In the outer-sphere reaction, electron transfer takes place in an activated complex (I-1) in which both metal ion complexes retain their full complement of coordinated ligands.



I-1

In the inner-sphere reaction, electron transfer occurs through an activated complex (I-2) in which one or more ligands in the first coordination sphere are shared between the two metal ion complexes.



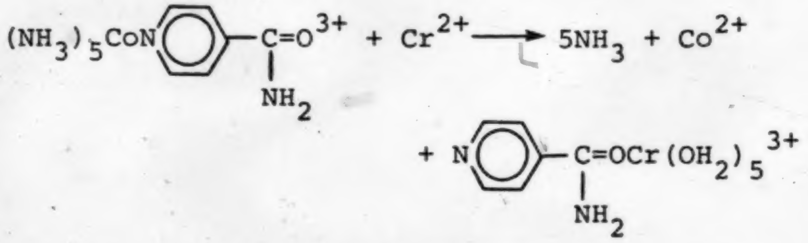
I-2

Distinguishing between these two types of reactions is not always a simple matter. If the rate of electron transfer is greater than the normal rates of ligand substitution for both metal ions, then the reaction must be of the outer-sphere type. On the other hand, if both reactants undergo substitution at rates greater than that of electron transfer, then either mechanism may be operative. In systems such as these, the mechanism of electron transfer can sometimes be deduced from a comparison of the kinetic results with those from established inner- and outer-sphere reactions. A system that most easily reveals the electron transfer mechanism is the reduction of complexes of the type $(NH_3)_5Co^{III}L$ by chromium(II). The oxidized forms of these ions (Co^{III} and Cr^{III}) are substitutionally inert whereas the reduced forms (Co^{II} and Cr^{II}) are substitutionally labile. As such, if $(H_2O)_5Cr^{III}L$ is isolated as the chromium(III) product of the reduction, this is compelling evidence that an activated complex of the type

$$[(NH_3)_5Co^{III}\text{-}L\text{-}Cr^{II}(OH_2)_5]^{\ddagger}$$

is formed. It is unlikely that the ligand transfer product $(H_2O)_5Cr^{III}L$ could be formed by reaction of free L with $Cr(OH_2)_6^{3+}$, owing to the kinetic inertness of the latter. Alternatively, if free L and $Cr(OH_2)_6^{3+}$ are found as products of the reaction, this suggests that an outer-sphere mechanism is operative. This assumes, of course, that $(H_2O)_5Cr^{III}L$ does not aquate rapidly relative to the electron transfer rate.

Electron transfer reactions have been the subject of numerous theoretical studies. Outer-sphere reactions have been examined by Libby,[2] Marcus,[3-8] Hush,[9] Levich and Dogonadze[10,11] and more recently by Schmidt[12,13] and Jortner _et al_.[14-16] The theory of inner-sphere electron transfer is somewhat more complicated but it has been examined qualitatively by George and Griffith,[17] Halpern and Orgel,[18] as well as by Burdett[19] and Larson.[20] Two limiting mechanisms of inner-sphere electron transfer have been proposed, chemical and resonance-transfer.[21] In the chemical mechanism, the electron transfers from the reducing agent to the ligand to form a ligand-centred radical intermediate. Finally, the electron passes from the ligand to the oxidizing centre. The formation of the radical intermediate requires that the ligand can be reduced. In contrast, when a resonance-transfer mechanism is operative, the electron is assumed to pass directly from a bound state on the reductant to another on the oxidant. Although no intermediate ligand-centred radical is formed, the bridging ligand is involved in the electron transfer reaction to the extent that it provides orbitals that mediate the electron between the two metal centres. The resonance-transfer mechanism is favoured when the incoming electron enters a metal orbital which can effectively overlap with orbitals on the bridging ligand. Such is the case for the chromium(II) reduction of many ruthenium(III) complexes.[22,23] Here the metal acceptor orbital is of $\pi(t_{2g})$ symmetry and can interact with low-lying π orbitals of the complexed ligand. On the other hand, for reactions such as



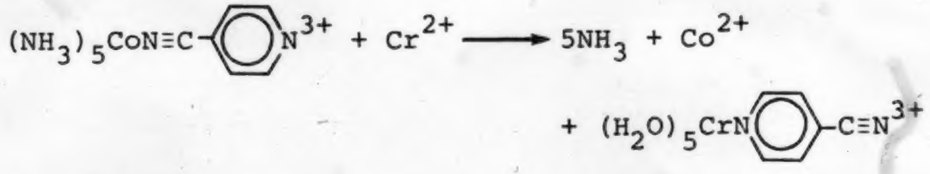
(1.2)

a resonance transfer mechanism is unlikely since empty ligand orbitals of σ symmetry which are needed to mix with the $\sigma(e_g)$ acceptor orbitals of cobalt(III) lie extremely high in energy.[24] However, reduction via a chemical mechanism might be expected to be facile owing to the ease of reduction of the isonicotinamide bridging ligand.

Whether a bridged or non-bridged activated complex is formed between an oxidant and a reductant depends in large part on the nature of the potential bridging ligand. Clearly, a minimum requirement for a ligand to serve as a bridge is the presence of at least two unshared electron pairs, since it must function as a Lewis base towards two metal cations. As such, the observation that $Cr(OH_2)_6^{3+}$ is the chromium(III) product of the reaction (1.3)

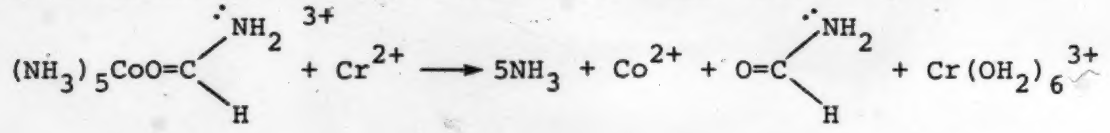
$$Co(NH_3)_6^{3+} + Cr^{2+} \longrightarrow 6NH_3 + Co^{2+} + Cr(OH_2)_6^{3+} \qquad (1.3)$$

is not surprising since only outer-sphere electron transfer is possible.[25] Coordinated ammonia has no second lone pair to coordinate chromium(II). On the other hand, ligand transfer product is detected in reaction (1.4).[26]

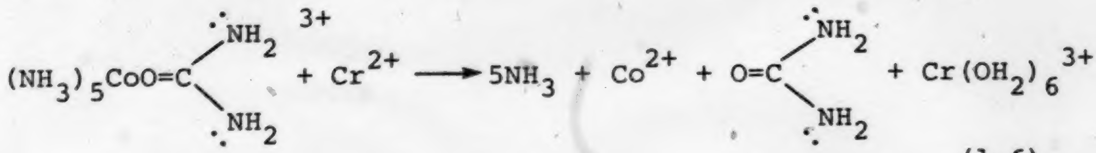


(1.4)

The lone pair of electrons on the pyridine nitrogen serves to bind the reductant, thereby allowing inner-sphere electron transfer to occur. However, the presence of a second lone pair of electrons is not a sufficient condition to guarantee that inner-sphere reduction will occur, as is evidenced by the reactions (1.5)[27] and (1.6).[28]

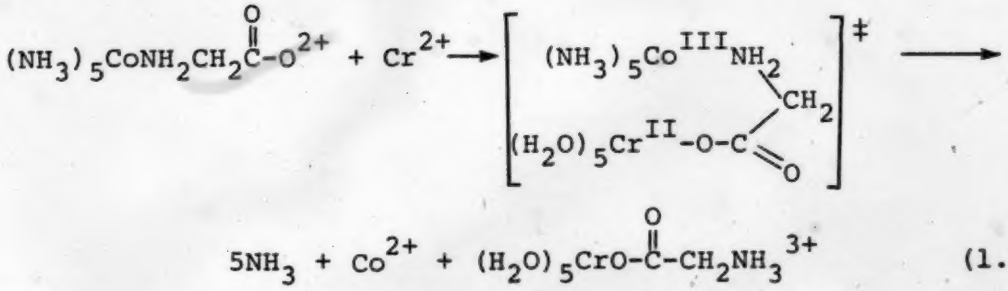


(1.5)



(1.6)

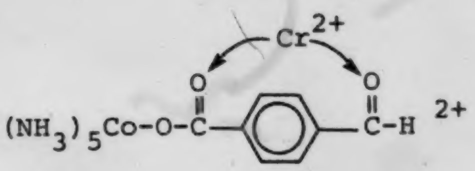
Outer-sphere reduction occurs despite the fact that basic sites are available for reductant binding. These systems differ from the others that do proceed by inner-sphere electron transfer in that coordination of chromium(II) at the available NH_2 functional groups yield activated complexes which do not possess a conjugated bonding system between oxidant and reductant. Observations of this type have caused some workers to suggest indirectly that a conjugated pathway between the two metal centres is an additional requirement for inner-sphere electron transfer.[27-29] Such a formulation requires a reassessment of the historically accepted definition of inner-sphere electron transfer. The problem is that the historical definition results in a series of electron transfer reactions which are unclassified with respect to their mechanism. An illustrative example of this latter class is provided by the reaction (1.7).[29]



(1.7)

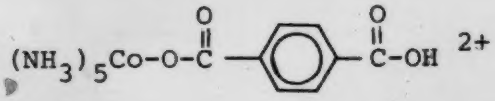
The reduction proceeds with ligand transfer to chromium(III) and as such, the reaction cannot be of the outer-sphere type. However, it does not conform to the inner-sphere definition just described since there is no conjugated ligand system between the two metal centres. This is an example of a reaction in which the bridging ligand serves only to bring oxidant and reductant into close proximity of one another in order to facilitate direct electron transfer between the two metal centres. Although the oxidant and reductant are bridged in the activated complex, the actual act of electron transfer is essentially of the outer-sphere type. Various names have been given to reactions such as (1.7): direct electron transfer,[18] linked electron transfer,[30] and precursor complexation formation with outer-sphere reduction.[29] A more precise name for this type of reaction is bridged-outer-sphere electron transfer since it more adequately describes the nature of both the activated complex and the electron transfer act itself. On this basis, outer-sphere reactions might be better regarded as non-bridged-outer-sphere electron transfer whereas inner-sphere reactions could be formulated as bridged-inner-sphere electron transfer.

When the bridging ligand offers more than one site for attachment of reductant, a distinction can be made between adjacent and remote attack. For complex I-3,[31]



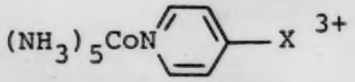
I-3

reduction by chromium(II) in principle can occur at either the coordinated carboxylate group (adjacent attack) or at the aldehyde function (remote attack). The kinetics and products suggest that I-3 is reduced by remote attack.[31] On the other hand, the reduction of I-4 by chromium(II)



I-4

is believed to occur by adjacent attack.[32] This mechanistic complication can arise with many bifunctional bridging ligands. The problem can be avoided by using either coordinated pyridine or nitrile bridging ligands such as



$(NH_3)_5CoN{\equiv}C\text{-}R^{3+}$

In both cases, adjacent attack cannot occur because of the lack of an unshared electron pair on the coordinated atom. This is one of several reasons why a study of the reactions of chromium(II) with simple nitrile complexes of $(NH_3)_5Co^{3+}$ has been undertaken.

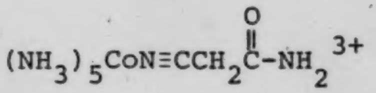
In order to gain information on the kinetic patterns that might distinguish bridged and non-bridged-outer-sphere electron transfer, the chromium(II) reduction of the following complexes have been studied:

$(NH_3)_5CoN{\equiv}CCH_3{}^{3+}$

I-5

$(NH_3)_5CoN{\equiv}CCH_2CH_2C{\equiv}N^{3+}$

I-6

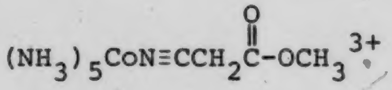


$(NH_3)_5CoN{\equiv}CCH_2\overset{\overset{O}{\|}}{C}{-}NH_2{}^{3+}$

I-7

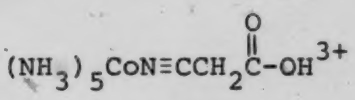
$(NH_3)_5CoN{\equiv}CCH_2C{\equiv}N^{3+}$

I-8



$(NH_3)_5CoN{\equiv}CCH_2\overset{\overset{O}{\|}}{C}{-}OCH_3{}^{3+}$

I-9



$(NH_3)_5CoN{\equiv}CCH_2\overset{\overset{O}{\|}}{C}{-}OH^{3+}$

I-10

With the exception of the acetonitrile complex I-5, all the complexes have ligands which contain remote functional groups capable of coordinating chromium(II). However, all the ligands contain at least one saturated methylene group, and as such, if ligand-transfer chromium(III) product is observed for any of these systems, a bridged-outer-sphere mechanism must be operative. The results of this study may add substantially to the understanding of the various factors that govern bridged-outer-sphere reduction.

Several workers have investigated the reactions of halogenated organic ligands with chromium(II).[33-35] Chromium(II) can function as a halogen abstractor in reactions of the type

$$RCH_2X + Cr^{2+} \longrightarrow \underset{\underset{(H_2O)_5CrX^{2+}}{+}}{RCH_2\cdot} \xrightarrow{Cr^{2+}} (H_2O)_5CrCH_2R^{2+} \qquad (1.8)$$

in which organochromium(III) complexes can be generated. In the present study, the reactions of chromium(II) with the following nitrile ligands have been studied:

$N{\equiv}CCH_2Cl$ I-11

$N{\equiv}CCH_2I$ I-12

In addition, the reactions of chromium(II) with the cobalt(III) complexes of these ligands

$(NH_3)_5CoN{\equiv}C\text{-}CH_2Cl^{3+}$ I-13

$(NH_3)_5CoN{\equiv}CCH_2I^{3+}$ I-14

have been examined. There are several ways in which these complexes can react with chromium(II). These nitrile complexes can undergo non-bridged-outer-sphere reduction.

$$(NH_3)_5CoN{\equiv}CCH_2X^{3+} + Cr^{2+} \longrightarrow 5NH_3 + Co^{2+} + N{\equiv}CCH_2X + Cr(OH_2)_6^{3+} \quad (1.9)$$

Alternatively, halogen abstraction can occur, according to the reaction

$$(NH_3)_5CoN{\equiv}CCH_2X^{3+} + Cr^{2+} \longrightarrow (NH_3)_5CoN{\equiv}CCH_2\cdot^{3+} + (H_2O)_5CrX^{2+} \quad (1.10)$$

This coordinated radical could undergo several reactions. It could react with a second equivalent of chromium(II) to produce the novel complex

$(NH_3)_5CoN{\equiv}CCH_2Cr(OH_2)_5^{5+}$

I-15

or the radical intermediate could dimerize according to the reaction

$$2(NH_3)_5CoN{\equiv}CCH_2\cdot^{3+} \longrightarrow (NH_3)_5CoN{\equiv}CCH_2CH_2C{\equiv}NCo(NH_3)_5{}^{6+} \qquad (1.11)$$

In addition, intramolecular electron tranfer might produce cobalt(II) and oxidation of the ligand according to the reaction

$$(NH_3)_5CoN{\equiv}CCH_2\cdot^{3+} \xrightarrow[H_2O]{} 5NH_3 + Co^{2+} + N{\equiv}CCH_2OH + H^+ \qquad (1.12)$$

A detailed study of the kinetics and products of these halogen abstraction reactions has been undertaken. The results elucidate the reaction pathways, products, and the kinetic effects of coordination and changing the halogen.

A detailed kinetic investigation also was undertaken of the reaction of chromium(II) with the fumaronitrile complex I-16.

$$(NH_3)_5CoN{\equiv}CCH{=}CHC{\equiv}N^{3+}$$

I-16

Unlike the nitrile complexes so far described, complex I-16 can undergo reduction by a bridged-inner-sphere mechanism, in which case the ligand transfer product would be expected to be

$$(H_2O)_5CrN{\equiv}CCH{=}CHC{\equiv}N^{3+}$$

I-17

However, it is also known that chromium(II) can reduce olefinic double bonds to yield either hydrogenated ligand or organochromium(III) complexes.[36,37] Kinetic and product studies have been undertaken on the chromium(II) reduction of free and coordinated fumaronitrile in order to establish the major reaction pathways and the effect of coordination on reactivity.

CHAPTER II

EXPERIMENTAL

Reagents

All solutions for kinetic studies were prepared with deionized water redistilled from alkaline permanganate in an all glass apparatus. Perchloric acid solutions were prepared by dilution of 70% perchloric acid (Allied Chemical, Ltd.) and standardized against sodium hydroxide. The sodium hydroxide solutions were prepared by dilution of ampoules of concentrated reagent (Fisher Scientific Co.). Solutions of lithium perchlorate (Alfa Products, Lts.) were filtered through a 0.22-μm Millipore filter (Millipore Corp.) and standardized by titration of the hydrogen ion released from a column of Dowex 50W-X8 cation-exchange resin.

Chromium(III) perchlorate solutions were prepared by reduction of primary standard potassium dichromate (B.D.H., Ltd.) with hydrogen peroxide in perchloric acid. The potassium perchlorate precipitate was removed by filtration through a 0.22-μm Millipore filter. The perchloric acid content was determined by treating 5 mL aliquots of the chromium(III) stock solution with 2.0 g of sodium oxalate (J.T. Baker Chemical Co.) in 50 mL of water. The solutions were heated to 70-80°C for

30 minutes during which time hexaaquochromium(III) is converted to tris(oxalato)chromium(III). After cooling to room temperature, the solutions were titrated potentiometrically (equivalence point ca. pH 7.8) with standard sodium hydroxide. For solutions requiring smaller acid concentrations, the chromium(III) stock solutions were treated with known amounts of lithium carbonate.

Chromium(II) solutions were prepared by reduction of chromium(III) solutions with amalgamated zinc (B.D.H., Ltd.). The chromium(II) content was determined by oxidation with an excess of standardized ammonium ferric sulfate solution (B.D.H., Ltd.). The excess iron(III) was determined by addition of potassium iodide (B.D.H., Ltd.) and titrating with a standard sodium thiosulfate solution. Sodium thiosulfate solutions were prepared by dilution of concentrated reagent (Fisher Scientific Co.).

Mercury(II) perchlorate solutions were prepared by weighing a known quantity of yellow mercuric oxide into a volumetric flask, adding a slight excess of perchloric acid and diluting to the mark. Any insoluble material was removed by filtration through a 0.22-μm Millipore filter.

Preparation of Complexes

Trifluoromethanesulfonic acid (Aldrich Chemical Co.) was used as supplied and handled by standard syringe techniques. Reagent grade acetone (Terochem Laboratories, Ltd.) and sulfolane (tetramethylene sulfone or 1,1-dioxothiolane) (Aldrich Chemical Co.) were stored over freshly heated (120°C) Davison 4A molecular sieves and were transferred with reasonable care to minimize exposure to atmospheric moisture. All other materials were of reagent grade and were used as supplied unless otherwise noted. Preparations in acetone or sulfolane were done in Erlenmeyer flasks closed with rubber serum stoppers.

The preparation of $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$, II-1, has been reported previously by Dixon *et al*.[38] and the utility of using this reagent as a starting material for the synthesis of pentaamminecobalt(III) complexes has been described. Reported here is an alternate preparation of II-1 which uses readily available and inexpensive reagents and makes efficient use of the trifluoromethanesulfonic acid.[39]

1. Aquopentaamminecobalt(III) Trifluoromethanesulfonate, $[(NH_3)_5CoOH_2](CF_3SO_3)_3$.

To a well-stirred solution of 150 mL of concentrated ammonia, 200 mL of water and 33 g of ammonium sulfate was added 60 g of cobalt(II) sulfate heptahydrate. Then 50 mL of 30% hydrogen peroxide was added slowly to the cobalt(II) solution while warming on a steam bath. Heating was continued for 2 h and then the solution was cooled and neutralized with 50% sulfuric acid. The solution was refrigerated overnight and the red crystalline product collected by filtration. The crude product was dissolved in 400 mL of warm water containing 40 mL of concentrated ammonia. The solution was filtered and neutralized with concentrated sulfuric acid. Neutralization is indicated by the colour change from reddish-purple $((NH_3)_5CoOH)^{2+}$ to reddish-orange $((NH_3)_5CoOH_2)^{3+}$. After cooling at ice temperature for several hours, the red crystalline product was collected by filtration, washed with ice-cold water and methanol, and air-dried to yield 40 g of product. This product has not been characterized fully, but sulfate analysis, as $BaSO_4$, and the molar extinction coefficient at 492 nm[40] are consistent with the formulation as $[(NH_3)_5CoOH_2](SO_4)(HSO_4)$.

The sulfate salt was converted to the trifluoromethanesulfonate salt by treatment with the stoichiometric amount of barium trifluoromethanesulfonate. The latter was prepared by slowly adding trifluoromethanesulfonic acid to an aqueous slurry of the required amount of barium carbonate until all of the carbonate dissolved. The sulfate salt (40 g) was dissolved in 400 mL of warm water (~60°) and the barium trifluoromethanesulfonate solution added slowly with stirring. The mixture was digested at 60-70° for about 1 h, then cooled to room temperature. The $BaSO_4$ was collected by filtration on a 0.22-μm Millipore filter. The filtrate was evaporated to dryness on a vacuum line while collecting the water in a large volume trap cooled in liquid nitrogen. Any excess CF_3SO_3H will be removed at this stage, and excess $Ba(CF_3SO_3)_2$, which may be present, does not affect subsequent preparations.

2. Trifluoromethanesulfonatopentaamminecobalt(III) Trifluoromethanesulfonate, $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$.

The aquopentaamminecobalt(III) trifluoromethanesulfonate complex loses water when heated at 100-110° *in vacuo* to yield trifluoromethanesulfonatopentaamminecobalt(III) trifluoromethanesulfonate, (II-1). The dehydration step has been carried out on 5-10 g samples either in a vacuum drying tube, or in a tube furnace. The dehydration seems to require 2-3 h, but routinely has been done overnight to ensure completion. The product has a pinkish-purple colour, and is reasonably stable toward hydration in air, although normally it has been stored in a desiccator over calcium sulfate. Anal. Calcd for $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$: C, 6.09; H, 2.56; N, 11.84. Found: C, 6.23; H, 2.55; N, 11.14.

3. Acetonitrile Complex, $[(NH_3)_5CoNCCH_3](ClO_4)_3$.

Into 12 mL of sulfolane was dissolved 2.6 g of $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$, (II-1), followed by the addition of 4 g of acetonitrile. The mixture was maintained at 45° for 1.5 h during which time the solution changed from red to bright orange. The solution was then cooled to room temperature, diluted with an equal volume of water and the complex isolated as its perchlorate salt by slow addition of perchloric acid. The complex was recrystallized twice from dilute perchloric acid. The solid obtained was washed with ethanol and diethyl ether, and air-dried. Anal. Calcd for $[(NH_3)_5CoNCCH_3](ClO_4)_3$: C, 4.97; H, 3.75; N, 17.38. Found: C, 4.95; H, 3.63; N, 16.82.

4. Cyanoacetamide Complex, $[(NH_3)_5CoNCCH_2C(O)NH_2](ClO_4)_3$.

A 1.7 g sample of cyanoacetamide was dissolved in 20 mL of a sulfolane solution containing 2-3 drops of CF_3SO_3H. Then 3 g of II-1 was added and the solution was stirred at room temperature overnight. The resulting orange solution was added slowly to 600 mL of a rapidly stirred solution of diethyl ether and sec-butanol (5:1). The complex was recrystallized from dilute perchloric acid and then subjected to cation-exchange chromatography at 5° on Dowex 50W-X2 in the H^+ form. The complex was eluted with 2 M NaCl (pH 4.5, acetic acid/sodium acetate buffer). The band of resin containing the desired product was separated physically and the product removed from the resin with 6 M HCl. The solution was treated with concentrated perchloric acid and cooled to 0° to obtain the perchlorate salt. The orange complex was recrystallized from dilute perchloric acid, washed with ethanol and ether, and air-dried.

Anal. Calcd for $[(NH_3)_5CoNCCH_2C(O)NH_2](ClO_4)_3$: C, 6.84; H, 3.64; N, 18.62. Found: C, 6.60; H, 3.64; N, 18.18.

5. Succinonitrile Complex, $[(NH_3)_5CoNCCH_2CH_2CN](ClO_4)_3$.

A 2 g sample of succinonitrile was dissolved in 20 mL of sulfolane to which had been added 4 g of II-1. After 4 h at room temperature, the orange reaction mixture was treated with 30 mL of water, followed by slow addition of concentrated perchloric acid. The viscous solid was allowed to settle at 0°C, filtered, and recrystallized from dilute perchloric acid. The product obtained was ion-exchanged on Dowex 50W-X2 resin, and the complex was isolated as described previously. The orange product was recrystallized from dilute perchloric acid, washed with ethanol and ether, and air-dried.

Anal. Calcd for $[(NH_3)_5CoNCCH_2CH_2CN](ClO_4)_3$: C, 9.19; H, 3.67; N, 18.76. Found: C, 9.14; H, 3.53; N, 18.74.

6. Methylcyanoacetate Complex, $[(NH_3)_5CoNCCH_2CO_2CH_3](ClO_4)_3$.

In a typical preparation, 4 g of II-1 was dissolved in 20 mL of sulfolane which contained 2-3 drops of CF_3SO_3H, and then 4 g of methylcyanoacetate was added. The reaction was allowed to proceed at room temperature for 6 h. Isolation of the product was achieved by diluting the reaction mixture with 30 mL of water, followed by the slow addition of perchloric acid with stirring. After cooling at 0°, the product was filtered off and recrystallized from dilute perchloric acid. The solid obtained was charged onto a column of Dowex 50W-X2 resin and isolated as described previously. The complex was recrystallized from dilute perchloric acid, washed with ethanol and ether, and air-dried.

Anal. Calcd for $[(NH_3)_5CoNCCH_2CO_2CH_3](ClO_4)_3$: C, 8.87; H, 3.72; N, 15.52. Found: C, 8.42; H, 3.55; N, 15.35.

Preparation of this complex in sulfolane with mild heating (40-45°C) reduced the reaction time to 2 h. The complex can also be prepared using acetone as solvent instead of sulfolane, and without the addition of CF_3SO_3H. The reaction time at room temperature was 10 h.

7. Cyanoacetic Acid Complex, $[(NH_3)_5CoNCCH_2CO_2H](ClO_4)_3$.

A 2.5 g sample of the methylcyanoacetate complex was dissolved in 70 mL of 3 M HCl and allowed to react at room temperature for 24 h. The reaction mixture was filtered and then treated with concentrated perchloric acid. After standing at 0° for several hours, the orange solid was collected and subjected to cation-exchange chromatography on Dowex 50W-X2 resin. The eluent concentration was increased from 0.25 M NaCl to 1.0 M NaCl (pH 4.8) in order to separate the cyanoacetate complex from the more easily eluted chloropentaamminecobalt(III) impurity, and from the more difficult to elute unreacted methylcyanoacetate complex. Treatment of the physically isolated cyanoacetate band with 6 M HCl removed the complex from the resin. Addition of concentrated perchloric acid effected precipitation of the desired complex. The product was recrystallized from dilute perchloric acid, washed with ethanol and ether, and air-dried. Anal. Calcd for $[(NH_3)_5CoNCCH_2CO_2H](ClO_4)_3$: C, 6.83; H, 3.44; N, 15.93. Found: C, 6.87; H, 3.40; N, 15.90.

8. Malononitrile Complex, $[(NH_3)_5CoNCCH_2CN](ClO_4)_3$.

Into 10 mL of sulfolane was added 2 g of freshly vacuum distilled malononitrile. The mixture was allowed to stand over molecular sieves for 4 h. The sieves were removed by filtration and 20 mL of sulfolane, 2.8 g of II-1 and 0.4 g of CF_3SO_3H were added to the filtrate with stirring. After standing for 18 h at room temperature, the bright orange solution was added slowly to 300 mL of rapidly stirred ether. The resulting oil was washed three times with ether by decantation and recrystallized from dilute perchloric acid. The product was dissolved in 0.1 M HBr, filtered, and 10 g of LiBr added to the filtrate. The solution was cooled and a pink impurity was removed by filtration. The filtrate was heated with solid $NaClO_4$ and after cooling, yielded a yellow precipitate which was collected by filtration. The treatment with HBr, LiBr and $NaClO_4$ was repeated. The resulting product was recrystallized from dilute perchloric acid, washed with ethanol and ether, and air-dried.

Anal. Calcd for $[(NH_3)_5CoNCCH_2CN](ClO_4)_3$: C, 7.08; H, 3.37; N, 19.28. Found: C, 7.22; H, 3.52; N, 19.25.

9. Chloroacetonitrile Complex, $[(NH_3)_5CoNCCH_2Cl](ClO_4)_3$.

A 3.3 g sample of freshly distilled chloroacetonitrile was dissolved in 40 mL of sulfolane containing molecular sieves. After standing for 4 h, the sieves were removed by filtration and 3 g of II-1, 0.5 g of CF_3SO_3H and an additional 20 mL of sulfolane were added. The solution was allowed to stand overnight at room temperature. The reddish-orange solution was added slowly to 500 mL of rapidly stirred ether. The oily residue obtained was washed three times with diethyl ether and air-dried. The product was dissolved in 0.01 M HCl, filtered and then precipitated by the addition of solid $NaClO_4$. The orange solid was recrystallized twice from dilute perchloric acid, washed with ethanol and ether, and air-dried.

Anal. Calcd for $[(NH_3)_5CoNCCH_2Cl](ClO_4)_3$: C, 4.64; H, 3.31; N, 16.23. Found: C, 4.54; H, 3.34; N, 15.93.

10. Iodoacetonitrile Complex, $[(NH_3)_5CoNCCH_2I](ClO_4)_3$.

The iodoacetonitrile ligand was prepared from chloroacetonitrile using the procedure of Merbach and Bünzli.[41] The cobalt(III) complex was prepared by dissolving 6 g of iodoacetonitrile into 20 mL of sulfolane containing molecular sieves. The solution was allowed to stand for 6 h. The molecular sieves were filtered off and 20 mL of sulfolane, 6 g of II-1 and 5 drops of CF_3SO_3H were added. The solution was allowed to stand at room temperature, and after 20 h, the mixture had partially reacted to form a reddish-orange solution and an orange precipitate. The solid was redissolved by addition of 20 mL of sulfolane and the reaction was allowed to proceed overnight at 40°C. The warm solution was added slowly to a stirred solution of 500 mL of ether. The resulting oil was washed three times with ether and air-dried. The residue was dissolved in 80 mL of 0.02 M HCl at 40°C, filtered, and perchloric acid added dropwise to affect precipitation. The yellow-orange solid was recrystallized from dilute perchloric acid, washed with ethanol and ether, and air-dried.

Anal. Calcd for $[(NH_3)_5CoNCCH_2I](ClO_4)_3$: C, 3.94; H, 2.81; N, 13.79. Found: C, 3.83; H, 2.81; N, 13.71.

11. Fumaronitrile Complex, $[(NH_3)_5CoNCCHCHCN](ClO_4)_3$.

A solution containing 4 g of II-1, 1.1 g of fumaronitrile and 2 drops of CF_3SO_3H in 20 mL of sulfolane was allowed to react at room temperature for 48 h. The resulting orange solution was added to a rapidly stirred mixture of 100 mL of 2-butanol and 500 mL of ether. The solid was collected by filtration, dissolved in 30 mL of 0.1 M HCl, and precipitated by addition of concentrated perchloric acid. The product was recrystallized from 0.1 M perchloric acid and then subjected to chromatography on Dowex 50W-X2 resin in the H^+ form. The product was separated from impurities by elution with 2 M NaCl (pH 4.5) and removed from the resin in a batch method with 6 M HCl. Concentrated perchloric acid was added to the HCl solution to precipitate the perchlorate salt. This was recrystallized from dilute perchloric acid, washed with ethanol and ether, and air-dried.

Anal. Calcd for $[(NH_3)_5CoNCCHCHCN](ClO_4)_3$: C, 9.23; H, 3.29; N, 18.84. Found: C, 9.21; H, 3.21; N, 18.67.

Subsequent work revealed that the ion-exchange step may be replaced by several recrystallizations from dilute perchloric acid. The complex can also be prepared using acetone as solvent without the addition of CF_3SO_3H.

Characterization of Complexes

Electronic Absorption Spectra

The wavelength maxima and extinction coefficients for the complexes synthesized are summarized in Table 1. Two observations should be noted. Firstly, the band maxima are at wavelengths more similar to those of nitrogen-bonded $(NH_3)_6Co^{3+}$ than to oxygen-bonded $(NH_3)_5CoOH_2^{3+}$. Secondly, an absorption maximum is observed at 467-468 nm for all the complexes regardless of whether the ligand has only nitrile functions or has a nitrile and another potential coordinating group. These results suggest that all the complexes are coordinated to cobalt(III) via the nitrile nitrogen. Indeed, the spectra closely resemble those of other nitrile complexes of $(NH_3)_5Co^{3+}$ reported previously.[42] For the cyanoacetamide complex, coordination through the amide nitrogen would be expected to yield a complex with maxima in the 478-486 nm region.[27,42] On the other hand, coordination via an oxygen atom of cyanoacetamide, cyanoacetate or methylcyanoacetate should yield a band maximum at a wavelength greater than 500 nm.[27,28,32,43,44] In addition, with respect to the latter system, coordinated ester complexes of $(NH_3)_5Co^{3+}$ appear

Table 1

Visible Absorption Spectra of Pentaamminecobalt(III) Complexes[a]

Complex	Visible Absorption Maxima λ_{max}, nm(ε, $M^{-1}cm^{-1}$)
$(NH_3)_5CoOH_2^{3+}$ [b]	492(47.5),346(44.5)
$(NH_3)_5CoNH_3^{3+}$ [b]	475(56.7),339(45.8)
$(NH_3)_5CoNCCH_3^{3+}$ [c]	468(60.4),335(52.6)
$(NH_3)_5CoNCCH_2C(O)NH_2^{3+}$	467(63.3),333(58.4)
$(NH_3)_5CoNCCH_2CH_2CN^{3+}$	467(60.7),333(54.4)
$(NH_3)_5CoNCCH_2CO_2CH_3^{3+}$	467(64.3),333(58.9)
$(NH_3)_5CoNCCH_2CO_2H^{3+}$ [d]	467(69.5),333(62.5)
$(NH_3)_5CoNCCH_2CN^{3+}$ [d]	467(62.9),334(63.6)
$(NH_3)_5CoNCCH_2Cl^{3+}$	467(62.4),333(56.8)
$(NH_3)_5CoNCCH_2I^{3+}$	468(66.7)
$(NH_3)_5CoNCCHCHCN^{3+}$	467(74.3)

[a] All spectra recorded in 0.50 M $HClO_4$ unless otherwise noted.

[b] Dixon, N.E.; Jackson, W.G.; Lancaster, M.J.; Lawrance, G.A.; Sargeson, A.M. Inorg. Chem. 1981, 20, 470.

[c] These values are in reasonable agreement with those reported: Jordan, R.B.; Sargeson, A.M.; Taube, H. Inorg. Chem. 1966, 5, 1091.

[d] These values are in fair agreement with those reported: Creaser, I.I.; MacB. Harrowfield, J.; Keene, F.R.; Sargeson, A.M. J. Am. Chem. Soc. 1981, 103, 3559.

to be labile to substitution.[44] The methylcyanoacetate complex isolated shows no such rapid decomposition in solution.

Infrared Spectra

The nitrile stretching frequencies of the complexes studied here are summarized in Table 2 along with the corresponding frequencies for the uncomplexed ligands. Coordination to cobalt(III) has increased the $\nu(C\equiv N)$ by 45-80 cm^{-1}. Similar behaviour has been observed in analogous systems[42,45] and is diagnostic of complex formation via the lone pair on the nitrile nitrogen.[46] Since this increase is observed in the cyanoacetamide, methylcyanoacetate and cyanoacetic acid complexes, this constitutes further evidence that the nitrile group and not other functions on the ligand are coordinated to cobalt (III). For the dinitrile substituted ligands succinonitrile, malononitrile and fumaronitrile, complexation produces two bands in the nitrile stretching region in agreement with a formulation in which one nitrile group is coordinated to cobalt(III) while the other remains uncomplexed. The lower energy vibrations observed for these complexes are very similar to those of the free ligands, and on this basis, were assigned to the uncoordinated nitrile functions.

Table 2

Nitrile and Carbonyl Stretching Frequencies for Some $(NH_3)_5Co^{3+}$ Complexes

	$\nu(C{\equiv}N), cm^{-1}$		$\nu(C{=}O), cm^{-1}$	
Ligand	Complexed[a]	Free Ligand	Complexed[a]	Free Ligand
$NCCH_3$	2337	2253[b]		
$NCCH_2Cl$	2323	2259[b]		
$NCCH_2I$	2300	2243[b]		
$NCCH_2C(O)NH_2$	2327	2271[a]	1722	1683[a]
$NCCH_2CO_2CH_3$	2333	2260[b]	1757	1750[b]
$NCCH_2CO_2H$	2325	2280[a]	1743	1728[a]
$NCCH_2CN$	2341,2272[c]	2272[a]		
$NCCH_2CH_2CN$	2328,2260[c]	2254[a]		
NCCHCHCN	2302,2240[c]	2240[a]		

[a] Spectra obtained using Nujol mulls and KBr disks.

[b] Spectra obtained as neat liquid.

[c] This is assigned to the uncoordinated C≡N from comparison to the free ligand.

Also given in Table 2 are the carbonyl stretching frequencies for coordinated and free cyanoacetamide, methylcyanoacetate and cyanoacetic acid. Coordination to cobalt(III) at either the oxygen or nitrogen in simple amides[43,47] or to oxygen in esters[44] and carboxylic acids[47,48] has been shown to result in appreciable low energy shifts (15-150 cm^{-1}) of the carbonyl stretching frequencies. In the present series, shifts to higher energy are observed. At least for methylcyanoacetate and cyanoacetic acid, the shifts are small (7-15 cm^{-1}) and probably arise from inductive effects brought on by coordination of cobalt(III) to the remote nitrile function. For cyanoacetamide, the high energy shift is somewhat larger (40 cm^{-1}). This may reflect a loss of intermolecular hydrogen bonding between amide groups upon coordination of the ligand to cobalt(III).

Finally, all of the complexes studied showed the characteristic vibrations of coordinated ammonia for pentaamminecobalt(III) in the 3300, 1630, 1350, and 830 cm^{-1} regions.[49]

NMR Spectra

The proton chemical shifts for the complexes studied are given in Table 3. Spectra of many of these complexes could be obtained only if acid was added to the DMSO-d_6 solvent. Sargeson and coworkers[50] found that complexes

Table 3

Proton NMR Data of Pentaamminecobalt(III) Complexes[a,b]

		τ	
Complex	trans NH_3	cis NH_3	Others
$(NH_3)_5CoNCCH_3{}^{3+}$	6.71	6.26	7.46(CH_3)
$(NH_3)_5CoNC(CH_2)_2CN^{3+}$	6.63	6.23	6.73-7.16(CH_2-CH_2)[c]
$(NH_3)CoNCCH_2C(O)NH_2{}^{3+}$	6.60	6.17	5.94(CH_2)
			2.50,2.28(NH_2)
$(NH_3)_5CoNCCH_2CO_2CH_3{}^{3+}$	6.61	6.21	5.70(CH_2)
			6.30(CH_3)
$(NH_3)_5CoNCCH_2CO_2H^{3+}$	6.68	6.26	5.70(CH_2)
$(NH_3)_5CoNC(CH)_2CN^{3+}$	6.56	6.22	3.15-2.48(CH=CH)[d]
$(NH_3)_5CoNCCH_2Cl^{3+}$	6.61	6.18	4.95(CH_2)
$(NH_3)_5CoNCCH_2I^{3+}$	6.53	6.13	5.81(CH_2)
$(NH_3)_5CoNCCH_2CN^{3+}$	6.50	6.12	5.1-5.2(CH_2)[e]

[a] Recorded in DMSO-d_6. Shifts relative to the residual solvent protons at 7.48 τ.

[b] 1-2 drops H_2SO_4 added.

[c] Complex multiplet due to non-equivalent $-CH_2-$ groups.

[d] Complex multiplet due to non-equivalent -CH- groups.

[e] Broadened resonance due to proton exchange.

containing an active methylene group readily deprotonate and that the carbanions generated undergo intramolecular electron transfer according to the reaction

$$(NH_3)_5CoNC\bar{C}HR^{2+} \longrightarrow 5NH_3 + Co^{2+} + NC\dot{C}HR$$

Addition of acid suppresses carbanion formation and subsequent decomposition.

All of the spectra exhibit resonances in the 6.1-6.3 τ and 6.5-6.7 τ regions with an intensity ratio of 4:1. These resonances are assigned to the *cis*- and *trans*-ammine protons, respectively. Other resonances in the spectra are readily assigned by comparison to the spectra of the free ligands. It is worth noting that broadening of the methylene resonances in the malononitrile (*ca*. 12 Hz) and cyanoacetic acid complexes (*ca*. 5 Hz) are observed, suggesting proton exchange with the added acid is occuring. The cyanoacetamide complex shows two distinct resonances at 2.28 and 2.50 τ which are assigned to the NH_2 protons of coordinated cyanoacetamide. The analogous resonances in the free ligand are observed at 2.38 and 2.69 τ. Two resonances are observed because partial double bond character causes restricted rotation around the C-N bond in the carboxamide function.[51]

The proton NMR spectrum of the succinonitrile complex is shown in Figure 1. In addition to the characteristic resonances of the *cis*- and *trans*-ammine protons, an A_2B_2

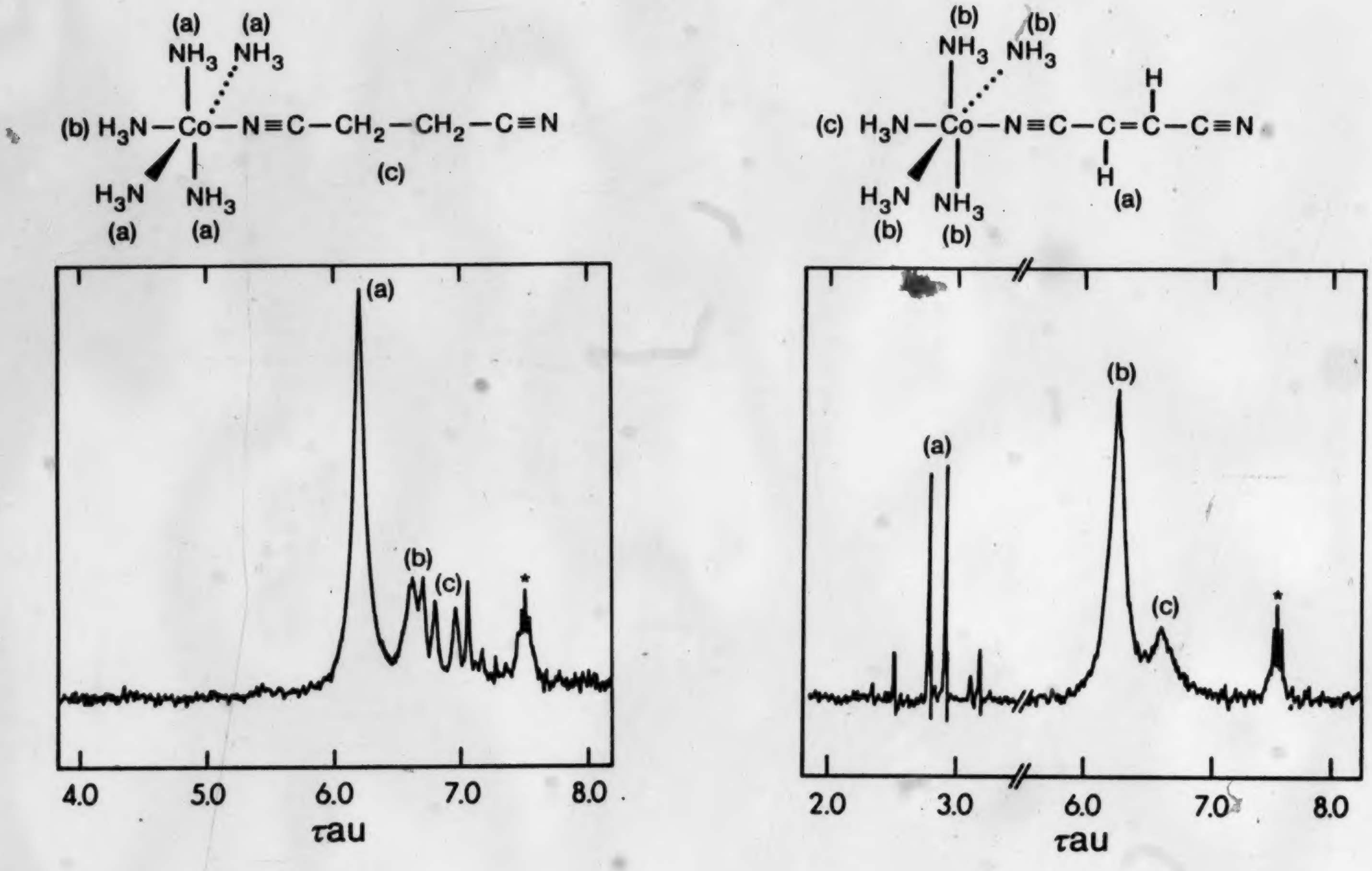


FIGURE 1. 60 MHz ^{1}H NMR spectra of $(NH_3)_5CoNCCH_2CH_2CN^{3+}$ and $(NH_3)_5CoNCCHCHCN^{3+}$ in d_6-dimethylsulfoxide.

spectrum[52] of the coordinated ligand is obtained. This arises because the chemical shift difference between the two $-CH_2-$ resonances is small relative to the coupling constant between them. However, a detailed analysis of the spectrum was not undertaken owing to the complexity of the splitting pattern and the fact that some of the resonances are masked by the trans-ammine protons at 6.63 τ.

Also shown in Figure 1 is the proton NMR spectrum of the fumaronitrile complex. Here an AB spectrum[53] is generated for the ligand protons. The coupling constant was found to be 16.5 Hz, which is characteristic of a trans arrangement around the double bond.[54] Therefore, the ligand has not isomerized during complexation to cobalt(III). The chemical shifts of the inequivalent protons were calculated to be 2.70 and 3.00 τ. Uncomplexed fumaronitrile exhibits a resonance at 3.16 τ, and on this basis, the low field resonance in the complex is assigned to the proton adjacent to the nitrile function coordinated to cobalt(III).

Kinetic Measurements

All chromium(II) reductions were done in solutions deoxygenated with high-purity argon and handled using standard syringe techniques. The kinetic data for the relatively slow reactions ($t_{1/2} \gtrsim 60$ s) were collected on a Cary 219 spectrophotometer equipped with a water-circulating temperature control system where water was passed from a thermostated water bath through the metal cell holder. Faster reactions were studied on an Aminco-Morrow stopped-flow apparatus modified in that two three-way Hamilton valves were added to the inlet system to permit anaerobic addition of reagents to the stopped-flow storage compartments. The drive syringes in the stopped-flow apparatus were thermostated with water circulated from a Colora constant temperature bath. The temperature was controlled by a Thermistemp Model 71 control device with the thermistor sensor in the temperature bath. The temperature was checked with a Doric Model DS-100-T3 digital readout thermometer coupled with a copper-constantan thermocouple which was periodically inserted into the storage syringe compartment.

Data from stopped-flow studies were analyzed by an analog comparison technique. The transmittance time curves were stored on a Tracor NS-570 signal averager and then output to a dual trace oscilloscope for comparison to a synthetic exponential decay curve. The time constant for the synthetic curve can be changed by varying the resistance in the circuit. The system was calibrated by recording synthetic curves on an X-Y recorder and calculating the rate constant in the usual manner. Values were within 1% of those expected from the resistance setting. An uncertainty of ±5% is expected in matching experimental and synthetic signals because of signal to noise levels.

For the chromium(II) reductions of the fumaronitrile complex of pentaamminecobalt(III), the initial rapid reaction necessitated monitoring the reaction under second-order conditions (the ratio of reductant to oxidant was less than 5:1). The low chromium(II) concentrations used required special precautions to avoid oxidation of the reductant. Degassing of solutions was achieved by passing high-purity argon through two chromium(II) scrubbers. To minimize the diffusion of oxygen into the argon flow, the argon was passed through tygon tubing that had previously been inserted inside thick-walled rubber tubing. Also, platinum syringe needles instead of the usual stainless steel needles were employed for both the degassing of solutions as well as the syringing of reagents.

The transmittance-time curves for this reaction were recorded on a Tektronix storage oscilloscope and were permanently recorded on Polaroid film. The rate constants were obtained from the equation

$$\ln\{1-[(1-b/a)((A_o-A_\infty)/(A_t-A_\infty))]\} = (b-a)kt + \ln(b/a) \quad (2.1)$$

where b is the initial reductant concentration, a is the initial oxidant concentration, k is the second-order rate constant (M^{-1} s^{-1}), and A_o, A_t and A_∞ are the absorbancies at t = 0, t and ∞, respectively.

For most of the reactions studied, pseudo-first-order conditions were employed (the ratio of reductant to oxidant is greater than 10:1). Where monophasic behaviour was observed, the observed rate constant was determined from the slope of a plot of $\ell n(A_t-A_\infty)$ versus time. Such plots were usually linear to more than 95% of reaction. In other systems, more complicated kinetic behaviour was observed and reaction schemes of the type

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{2.2}$$

and

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \tag{2.3}$$

were required to explain the data. There is no simple equation from which the rate constants and extinction coefficients of the various species can be calculated directly from the data. Such data were handled using the procedures described in Appendix A.

The activation parameters were obtained using the transition-state equation

$$\ell n(k/T) = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R + \ell n(\kappa k_B/h) \tag{2.4}$$

where k is the specific rate constant, k_B is Boltzmann's constant, R is the gas constant, κ is the transmission coefficient which is assumed to be equal to 1, h is Planck's constant, T is the temperature in °K, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation, respectively. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by non-linear least-squares fitting of the kinetic data at these temperatures to equation (2.4).

Analyses

Elemental analyses for C, H and N were performed by the Microanalytical Laboratory at the University of Alberta Chemistry Department. Special analytical procedures are described below.

Cobalt:

The percent cobalt in a cobalt(III) complex was determined by the method of Kitson.[55] A sample containing about 0.02 mmole of cobalt(III) was dissolved in 5 mL of 0.1 M NaOH and hydrolyzed near 80° for several hours. The solution was cooled, 2.0 mL of concentrated HCl added and heating continued for 20-30 minutes. After cooling, 2.5 mL of 50% aqueous NH_4SCN and 25 mL of acetone were added. The solution was brought to 25°, diluted to 50 mL with water and the absorbance at 622 nm recorded. The amount of cobalt present was calculated using the molar extinction coefficient of 1786 M^{-1} cm^{-1}.

The determination of the amount of cobalt(II) in an unknown sample was ascertained as above, except that the base hydrolysis reaction and heating were omitted.

Chromium:

The chromium concentrations of solutions were determined spectrophotometrically after conversion to chromate. The oxidation of chromium(III) species were carried out in basic solution (final solution 1.0 M in NaOH) with hydrogen peroxide. Excess hydrogen peroxide was destroyed by boiling the solution. The chromium concentration was determined from the absorbance at 372 nm where the extinction coefficient of CrO_4^{2-} is 4.815×10^3 M^{-1} cm^{-1}.

Stoichiometry and Product Analysis

The stoichiometries of the chromium(II) reductions were determined by analyzing for the chromium(II) left after complete reaction of the limiting oxidant. The amount of chromium(II) remaining was ascertained by its reaction with excess iron(III) which was determined iodometrically.

The products of reaction were separated using ion-exchange techniques. Dowex 50W-X2, Dowex 50W-X8 and Sephadex SP-C25 cation-exchange resins were used. The first two resins were pretreated with 6 M $HClO_4$, distilled water, 2 M NaOH/1% H_2O_2, distilled water, 6 M $HClO_4$, distilled water, 50% aqueous acetone, ethanol and distilled water. The latter resin was pretreated similarly, except 2 M $HClO_4$ and 1 M NaOH/1% H_2O_2 were used.

Reaction mixtures were charged onto columns maintained at 2° and the initial eluent collected and analyzed for free ligand, where possible. Elution was achieved by gradually increasing the concentration of $NaClO_4$ and $HClO_4$ in the eluting solution until separation into discrete bands was achieved. The bands were eluted off the column and characterized spectrophotometrically on a Cary 219 spectrophotometer.

The molar extinction coefficients of the products were calculated on the basis of the chromium or cobalt concentrations which were determined as described previously.

Instrumentation

All visible and ultraviolet spectra were recorded using a Cary 219 spectrophotometer. Proton magnetic resonance spectra were obtained using Varian A56/60 or Bruker WH-400 spectrometers. ^{13}C NMR spectra were recorded using a Bruker WH-200 spectrometer. Infrared spectra were recorded in KBr pellets and Nujol mulls on a Nicolet-FT-7000 spectrophotometer. The pH measurements were made on either a Beckman Expandomatic or a Metrohm Herisau pH meter.

CHAPTER III

Chromium(II) Reduction of Cyanoacetate Complexes of $(NH_3)_5Co^{3+}$.

Introduction

The chromium(II) reductions of several nitrile complexes of the general type $(NH_3)_5CoNCCH_2R^{3+}$, where R = H, CN, CH_2CN, $C(O)NH_2$, CO_2CH_3 and CO_2H, have been studied. Since adjacent attack at the nitrile function is not possible and since there is a saturated CH_2 between the nitrile and R functions, the results would be expected to reflect substituent effects on non-bridged-outer-sphere reactions. However, bridged-outer-sphere reduction for all but the acetonitrile complex is possible as well. In addition, Sargeson and coworkers[50] have shown that the active methylene group in the cyanoacetate systems can lead to internal oxidation-reduction and electrophilic attack on these ligands. The active methylene group might also influence the chromium(II) reduction reactions.

Experimental

The syntheses of the pentaamminecobalt(III) complexes studied here have been described in Chapter II.

Acid Dissociation Constant of $(NH_3)_5CoNCCH_2CO_2H^{3+}$.

Spectrophotometric measurements were carried out at 260 nm at 14.6, 25.0, and 35.0°C at an ionic strength of 0.50 M $(LiClO_4-HClO_4)$. From 11 to 15 acidities in the range 0.0008-0.495 M were studied at each temperature. Observations were made in a 5 cm path length cell at a cobalt(III) concentration of 7.67×10^{-4} M, and in one case, at 25.0°C and [cobalt(III)] = 2.39×10^{-3} M. The data, which are listed in Table C-1 of Appendix C, were fitted by non-linear least-squares to the theoretical equation derived in Appendix B. At 14.6, 25.0, and 35.0°C, the extinction coefficients $(M^{-1}\ cm^{-1})$ of the acidic and basic forms were found to be 35.4 and 113.4, 37.3 and 127.6, and 52.6 and 149.3, respectively. The values are temperature dependent because they are on the side of a charge-transfer band. The acid dissociation constants at 14.6, 25.0 and 35.0°C are $(3.42 \pm 0.43) \times 10^{-2}$, $(3.58 \pm 0.27) \times 10^{-2}$, and $(3.53 \pm 0.34) \times 10^{-2}$ M, respectively.

Product Analysis

After the reductions of the cobalt(III) complexes were complete, the excess chromium(II) was air oxidized and the solution subjected to ion-exchange chromatography at 5°C on Dowex 50W-X2. The free organic product was collected in the initial eluent, and the cobalt(II) and chromium(III) species were eluted with a solution of increasing concentration from 0.12 M $NaClO_4$ in 0.025 M $HClO_4$ to 0.50 M $NaClO_4$ in 0.10 M $HClO_4$. Chromium-containing fractions were characterized as described previously in Chapter II.

The free organic products collected in the initial eluent were determined by a modification of the procedure of Lovelady.[56] Two milliliters of aqueous sulfanilic acid (1.2×10^{-2} M in 0.36 M HCl) in a 10.0 mL volumetric flask were cooled in a refrigerator, and 0.20 mL of 1.2 M $NaNO_2$ was added. The solution was allowed to stand in the refrigerator for 10 min, and then it was treated with 1 mL of 6 M NaOH and an aliquot of the nitrile solution. The solution was diluted to 10 mL at room temperature and the absorbance was recorded at 490 nm, 2.5 min after adding the nitrile solution. Tests showed that Beer's law was obeyed for up to 2.44 $\mu g\ ml^{-1}$ of cyanoacetic acid and for up to 3.30 $\mu g\ ml^{-1}$ of cyanoacetamide. Since the colour is not very stable, the analyses were always done in parallel with solutions of known concentration. However, the results were quite reproducible from day to day if the same procedure was followed strictly. Since ethylcyanoacetate is known to hydrolyze rapidly[57] in the basic conditions of the analysis, the methyl ester was assumed to be similarly reactive, and cyanoacetic acid standards were used for comparison in the ester analysis. This procedure was found to be unsatisfactory for the determinations of acetonitrile and succinonitrile.

Results

The rates of the chromium(II) reductions of the acetonitrile, succinonitrile, cyanoacetamide and methylcyanoacetate complexes of pentaamminecobalt(III) were found to be independent of the hydrogen ion concentration, and obeyed the rate law

$$\frac{-d[\mathrm{cobalt(III)}]}{dt} = k[\mathrm{cobalt(III)}][\mathrm{chromium(II)}] \qquad (3.1)$$

The kinetic data are given in Table C-2 of Appendix C. A summary of the rate constants and activation parameters is given in Table 4.

The reaction products of solutions which were air oxidized after 10 half-lives were determined by ion-exchange chromatography on Dowex 50W-X2 resin. The results are given in Table 5. The chromium(III) product in each case was identified as $Cr(OH_2)_6^{3+}$ on the basis of its visible absorption spectrum which has maxima at 407 and 574 nm with extinction coefficients of 15.6 and 13.4 M^{-1} cm^{-1}, respectively.[58] Essentially quantitative recovery of free ligand and $Cr(OH_2)_6^{3+}$ was observed for the cyanoacetamide and methylcyanoacetate systems. The high yield of chromium(III) is due to the production of some $Cr(OH_2)_6^{3+}$ during the air-oxidation of excess chromium(II). Because of the lack of a satisfactory method of analysis for free acetonitrile and succinonitrile, the amount of free ligand

Table 4

Rate Constants and Activation Parameters for the Reduction of Nitrile Complexes of Pentaamminecobalt(III) by Chromium(II).

Temperature	$10^2 \times k$, $M^{-1}s^{-1}$ [a,b]			
°C	$NCCH_3$	$NC(CH_2)_2CN$	$NCCH_2CONH_2$	$NCCH_2CO_2CH_3$
25°	0.943(0.944)	2.54(2.52)	2.61(2.58)	2.34(2.34)
35°	1.73(1.71)	4.35(4.40)	4.25(4.37)	4.07(4.06)
45°	3.04(3.05)	7.72(7.67)[c]	7.40(7.27)	6.96(6.96)
$\Delta H^{\dagger}$ kcal mol^{-1} [d]	10.3±0.4	9.5±0.4	9.0±0.6	9.5±0.5
$\Delta S^{\dagger}$ cal $mol^{-1}deg^{-1}$ [d]	-33.1±1.4	-34.1±1.1	-35.6±1.9	-34.2±1.3

[a] Ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Values in parentheses are calculated from the least-squares fit to the transition-state theory equation.

[c] The temperature is actually 45.9°.

[d] Errors quoted are 95% confidence limits, and are about three times larger than one standard deviation.

Table 5

Product Distribution for the Reduction of Nitrile Complexes of $(NH_3)_5Co^{3+}$ by Chromium(II).

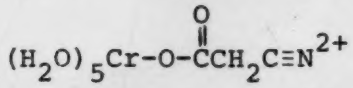
			Reactant Concentration, M			Product Distribution,[a] %[b]	
Ligand	Temp, °C	Rx. Time, min	10^3x [Co(III)]	10^2x [Cr(II)]	$[H^+]$	Ligand	$Cr(OH_2)_6^{3+}$
$NCCH_2CH_2CN$	25.0	600	7.86	1.24	0.100	-	98
$NCCH_2CONH_2$	25.0	66	9.66	5.85	0.097	95.3±2.5	-
	5.0	480	7.75	3.72	0.100	96.5±2.5	111
$NCCH_2CO_2CH_3$	25.0	162	7.54	3.72	0.100	106±2.4	123

[a] Chromium(III) product was determined by ion-exchange separation and oxidation to CrO_4^{2-}. Free ligand was determined in the initial eluant from ion-exchange separation by the sulfanilic acid test.

[b] Based on total number of moles of cobalt(III) complex.

liberated could not be determined in these systems. However, practically complete recovery of $Cr(OH_2)_6^{3+}$ was observed for the succinonitrile complex.

The reduction of the cyanoacetic acid complex is qualitatively different from that of the four systems described above. The reaction is considerably faster and a major product is a dipositive chromium(III) complex. This species was separated from $Cr(OH_2)_6^{3+}$ by ion-exchange chromatography on Dowex 50W-X2, and was found to have absorbance maxima at 411 and 570 nm with extinction coefficients of 22.4 and 22.3 M^{-1} cm^{-1}, respectively. This spectrum is essentially the same as that of $(H_2O)_5CrO_2CCH_3^{2+}$,[59] and serves to identify the product as



$$(H_2O)_5Cr{-}O{-}\overset{O}{\overset{\|}{C}}CH_2C{\equiv}N^{2+}$$

III-1

The kinetic results for the chromium(II) reduction of $(NH_3)_5CoNCCH_2CO_2H^{3+}$ are summarized in Table C-3 of Appendix C. The reaction is first-order in oxidant and reductant, and the second-order rate constant (k_{obsd}) increases with decreasing $[H^+]$. However, a plot of $(k_{obsd})^{-1}$ versus $[H^+]$ is not linear as shown in Figure 2. The direction of the curvature is consistent with the rate law

$$k_{obsd} = \frac{a[H^+] + b}{c + [H^+]} \qquad (3.2)$$

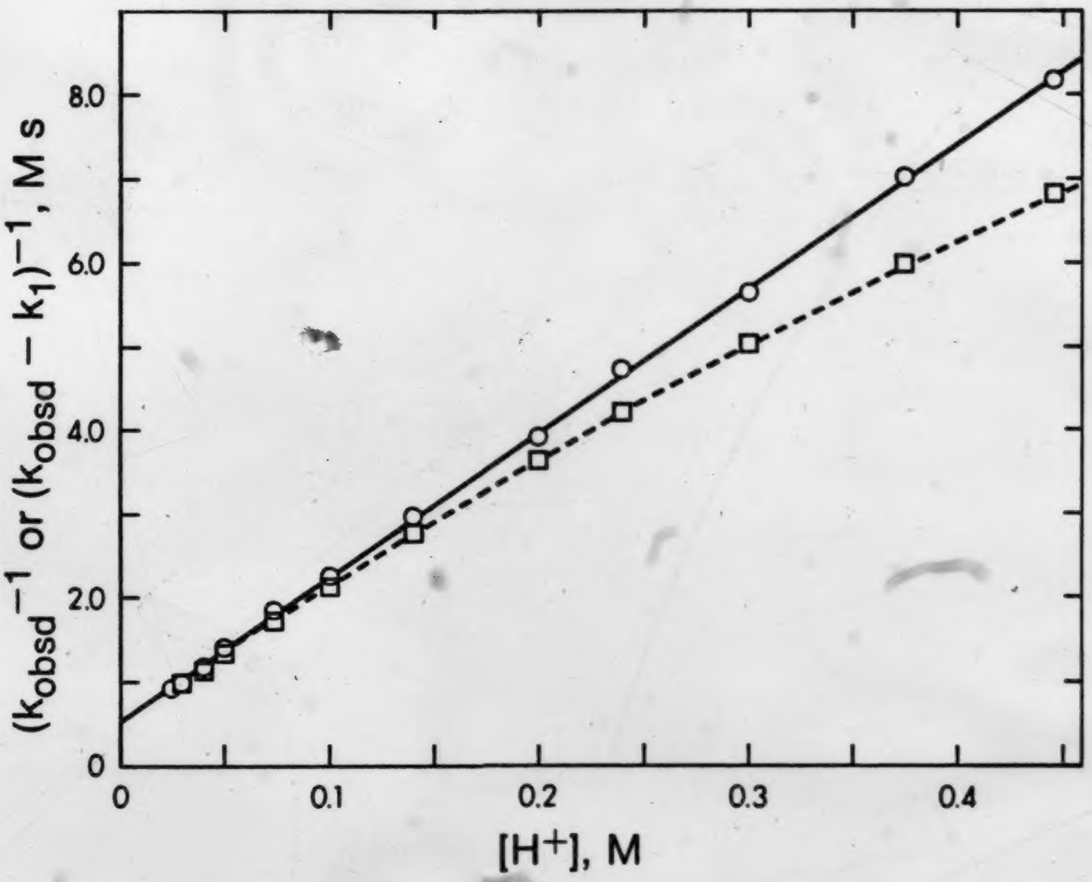


FIGURE 2. Variation of k_{obsd}^{-1} (□) and $(k_{obsd} - k_1)^{-1}$ (○) with $[H^+]$ for the reduction of $(NH_3)_5CoNCCH_2CO_2H^{3+}$ by Cr^{2+} at 25°C in 0.50 M $LiClO_4$-$HClO_4$. The value of $k_1 = 2.34 \times 10^{-2}$ M^{-1} s^{-1} was taken from the reduction of the ester complex. The dashed curve is an eye guide only.

The plot should be linear if a = 0, but the magnitude of the curvature is not large enough to allow a realistic evaluation of "a". Nevertheless, the form of the rate law is consistent with the following reaction scheme:

$$\begin{tikzcd}
(NH_3)_5CoNCCH_2CO_2H^{3+} \arrow[r, shift left, "K_a"] \arrow[d, "k_1"', "Cr^{2+}"] & (NH_3)_5CoNCCH_2CO_2^{2+} + H^+ \arrow[l, shift left] \arrow[d, "k_2"', "Cr^{2+}"] \\
Cr(OH_2)_6^{3+} + NCCH_2CO_2H + Co^{2+} + 5NH_3 & (H_2O)_5CrO_2CCH_2CN^{2+} + Co^{2+} + 5NH_3
\end{tikzcd} \qquad (3.3)$$

This scheme predicts that the ligand-transfer product $(H_2O)_5CrO_2CCH_2CN^{2+}$ arises solely from reduction of the unprotonated cobalt(III) complex and that $Cr(OH_2)_6^{3+}$ and free cyanoacetic acid are formed from the protonated complex.

The predicted rate law gives the following second-order rate constant

$$k_{obsd} = \frac{k_1[H^+] + k_2K_a}{K_a + [H^+]} \qquad (3.4)$$

which has a form consistent with the experimental rate law (equation (3.2)). Unfortunately, the value of k_1 (=a) cannot be established from the data, but the reaction scheme leads to the expectation that k_1 should be similar to the rate constant for the corresponding ester or amide complexes. These complexes have the same charge, similar structure and are reduced without ligand-transfer to chromium. In addition, the ester and amide have very similar rate constants for reduction (Table 4). If k_1 is assumed to be equal to the rate constant for reduction of the ester, then a plot of $(k_{obsd} - k_1)^{-1}$ versus $[H^+]$ should be linear as shown in Figure 2. Since the k_1 correction to k_{obsd} is about 15% at most, it makes no real difference whether the ester or amide rate constants are used. With k_1 fixed at the values for the ester, a least-squares analysis of the data gives the values for k_2 and K_a shown in Table 6.

The proposed reaction scheme can be tested by independently measuring the acid dissociation constant of $(NH_3)_5CoNCCH_2CO_2H^{3+}$. This was done spectrophotometrically, as described in the Experimental Section. Unfortunately, the only significant difference in the spectra of the protonated and unprotonated forms occurs on the side of the charge transfer band. At the wavelength used, 260 nm, the absorbance of the protonated form is only moderately dependent on wavelength, but for the unprotonated form, the absorbance is increasing rapidly with decreasing wavelength. Although these are far from ideal conditions for a spectrophotometric analysis, the data can be fitted so that observed and calculated extinction coefficients agree within 1%. The results are shown in Table C-1 of Appendix C. The values of K_a obtained at the three temperatures

TABLE 6.

Kinetic Results for the Reduction of N-bonded Cyanoacetatopenta-amminecobalt(III) by Chromium(II).[a]

Temperature	$10^2 \times k_1$,[b] $M^{-1}\ s^{-1}$	k_2, $M^{-1}\ s^{-1}$	$10^2 \times K_a$, M	
14.9	1.29	0.903±0.053	3.02±0.20	3.42±0.43[c,d]
25.0	2.34	2.11±0.10	2.73±0.17	3.58±0.27[c]
35.0	4.06	4.00±0.35	2.81±0.32	3.53±0.34[c]
$\Delta H^\dagger$ kcal mol^{-1} [e]		12.5±1.1		
$\Delta S^\dagger$ cal mol^{-1} deg^{-1} [e]		-15.2±3.6.		
ΔH° kcal mol^{-1} [e]			-0.74±1.44	
ΔS° cal mol^{-1} deg^{-1} [e]			-9.6±4.7	

[a] Errors quoted are 95% confidence limits.

[b] Values for the reduction of the methyl ester complex, held constant during the data analysis.

[c] Values obtained from the spectrophotometric study.

[d] Value at 14.6°.

[e] Values obtained by simultaneously fitting all the data at three temperatures.

are given in Table 6.

The agreement between the spectrophotometric and kinetic K_a values (Table 6) is considered satisfactory. The spectrophotometric values are about 20% larger, but the values at 14.9° and 35.0° agree within their respective confidence limits. It should be noted that the spectrophotometric values are concentration constants, and comparison to the kinetic values involves the assumption that the ratio of the activity coefficients of the protonated and unprotonated forms remain constant as the medium is changed from essentially 0.5 M $HClO_4$ to 0.5 M $LiClO_4$.

The proposed reaction scheme was also tested by comparing the experimental product distribution to that predicted from the rate constants k_1 and k_2. The results obtained are given in Table 7 and show that the fraction of ligand-transfer product increases as the acidity decreases. Since independent experiments have shown that the ligand-transfer product is stable to aquation under the experimental conditions employed, this observed product variation with acidity must represent a change in the product distribution from the reduction reaction. The tabulated results show that there is good agreement between the predicted and observed amounts of ligand-transfer product. The small differences observed may be due to the uncertainty in k_1, or possibly to some reduction of the

Table 7

Product Distribution from the Chromium(II) Reduction of Pentaamminecobalt(III) Cyanoacetate.

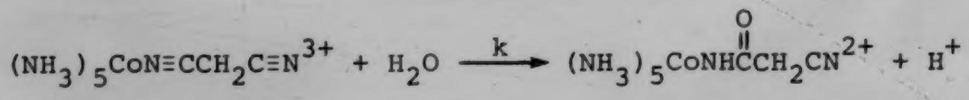
Reactant Concentrations, M			Product Distributions, %[a,b]	
$[H^+]$	$10^3 x[Co(III)]$	$10^2 x[Cr(II)]$	$(H_2O)_5CrO_2CCH_2CN^{2+}$	$NCCH_2CO_2^-$
0.400	4.56	1.41	82.9(86)	19.8(14)
0.300	7.76	1.56	85.1(89)	-
0.300	7.78	1.58	85.7(89)	-
0.050	2.99	0.93	99.2(98)	8.2(2)

[a] Chromium(III) product was determined by ion-exchange separation and oxidation to CrO_4^{2-}. The free cyanoacetate was determined in the initial eluant from ion-exchange separation by the sulfanilic acid test.

[b] Values in parentheses are calculated from the kinetic parameters and the proposed reaction scheme.

unprotonated complex by a non-bridged-outer-sphere path. If this outer-sphere path has the same rate constant as the ester, then the ligand-transfer percentage is lowered by about 1% at each acidity. In any case, the results support the proposed reaction scheme.

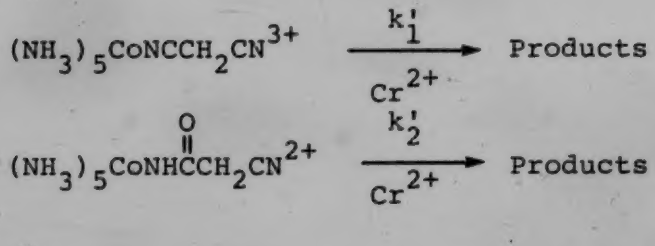
Preliminary studies on the chromium(II) reduction of the malononitrile complex, $(NH_3)_5CoNCCH_2CN^{3+}$, were also undertaken. The semi-logarithmic plots of the absorbance change at 467 nm versus time were non-linear. This is attributed to the presence of some carboxamide complex formed by hydrolysis of the coordinated nitrile (k = 1.0×10^{-4}, 25°C, pH 1-3, 1.0 M $NaClO_4$)^{60} according to reaction (3.5).



$$(NH_3)_5CoN{\equiv}CCH_2C{\equiv}N^{3+} + H_2O \xrightarrow{k} (NH_3)_5CoNH\overset{\overset{O}{\|}}{C}CH_2CN^{2+} + H^+$$

(3.5)

The carboxamide complex may form during the preparation and degassing of reactant solutions, and small amounts may also be present in the original sample. Therefore, the absorbance data were fitted to scheme (3.6)



$$(NH_3)_5CoNCCH_2CN^{3+} \xrightarrow[Cr^{2+}]{k_1'} \text{Products}$$

$$(NH_3)_5CoNH\overset{\overset{O}{\|}}{C}CH_2CN^{2+} \xrightarrow[Cr^{2+}]{k_2'} \text{Products}$$

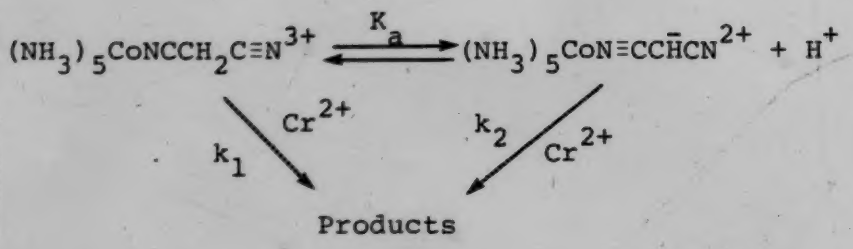
(3.6)

for which the general mathematical derivation is given in

Appendix A. The kinetic results are summarized in Table C-4 of Appendix C. It is estimated that 10 to 20% of the carboxamide would form during reagent preparation so that the reaction with the larger absorbance change was assigned to reduction of the nitrile complex. The reduction of the malononitrile complex is first order in oxidant and reductant and the second-order rate constant (k_1') increases with decreasing [H^+], obeying the rate law

$$k_1' = a + \frac{b}{[H^+]} \tag{3.7}$$

The rate law is consistent with the following reaction scheme:



$$\begin{tikzcd} (NH_3)_5CoNCCH_2C\equiv N^{3+} \arrow[rr, shift left, "K_a"] \arrow[dr, "Cr^{2+}", "k_1"'] & & (NH_3)_5CoN\equiv CC\bar{H}CN^{2+} + H^+ \arrow[ll, shift left] \arrow[dl, "k_2"', "Cr^{2+}"] \\ & \text{Products} & \end{tikzcd}$$

(3.8)

The proposed mechanism yields the rate law

$$k_1' = \frac{k_1[H^+] + k_2K_a}{K_a + [H^+]} \tag{3.9}$$

However, it is known that the acid dissociation constant for the malononitrile complex is small[60] in comparison to the acid concentrations (0.039-0.393 M) of the present study so that equation (3.9) reduces to

$$k_1' = k_1 + \frac{k_2K_a}{[H^+]} \qquad (3.10)$$

which is of the same form as that obtained experimentally (equation (3.7)). The calculated values of k_1 and k_2K_a are $(6.29 \pm 0.29) \times 10^{-2}\ M^{-1}\ s^{-1}$ and $(1.40 \pm 0.19) \times 10^{-3}\ s^{-1}$ (25°C, 0.50 M $LiClO_4$-$HClO_4$), respectively. Assuming that the pK_a of the complex is 5.7,[60] the value of k_2 is estimated to be $(7.0 \pm 1.0) \times 10^{2}\ M^{-1}\ s^{-1}$.

Despite the relatively large scatter in the values of k_2' for the parallel second reaction, the reduction of the carboxamide complex appears to be first-order in both oxidant and reductant and independent of the acid concentration. The value for k_2' was determined to be $(1.01 \pm 0.15) \times 10^{-2}\ M^{-1}\ s^{-1}$ (25°C, 0.50 M $LiClO_4$-$HClO_4$).

A preliminary product study was undertaken. A solution of $(NH_3)_5CoNCCH_2CN^{3+}$ (4.9×10^{-3} M) in 0.050 M $HClO_4$ was allowed to react for 70 minutes with chromium(II) (2.0×10^{-2} M). During this time, essentially all of the malononitrile complex should undergo reduction whereas most of the carboxamide complex will remain unreacted. The reaction mixture was air-oxidized and charged onto a column of Dowex 50W-X2. Although no attempt was made to quantify the results, large amounts of cobalt(II) were detected and the sole chromium(III) product was $Cr(OH_2)_6^{3+}$.

In addition, a small amount of a yellowish-pink material was detected. Although the fraction was contaminated with $Cr(OH_2)_6^{3+}$, its electronic spectrum in 0.50 M $HClO_4$ revealed maxima at 481 and 345 nm, in good agreement with the previously reported spectrum of $(NH_3)_5CoNHC(O)CH_2CN^{2+}$ in 0.01 M NaOH.[60] These observations indicate that the carboxamide nitrogen is not significantly protonated in 0.50 M $HClO_4$, due to the electron-withdrawing $-CH_2CN$ substituent.

Discussion

The kinetic parameters for the chromium(II) reductions of the pentaamminecobalt(III) nitrile complexes studied here, as well as some by other workers, are given in Table 8. For most of these systems, the rate constants are remarkably constant at (2.3 ± 0.3) x 10^{-2} M^{-1} s^{-1} with correspondingly similar activation parameters. The rate constant given for the benzonitrile complex will also fit this pattern if the ionic strength effect on the rate is the same as that found for the acetonitrile and cyanoacetamide complexes. Only the malononitrile and cyanoacetate anion complexes, which will be discussed separately, and the acetonitrile complex deviate from this pattern.

The invariant nature of the rate constants and activation parameters imply that a common mechanism may be operative for these systems. Indeed, product analysis experiments on these systems have shown that the products of reaction are always free ligand and $Cr(OH_2)_6^{3+}$, indicative of a non-bridged-outer-sphere mechanism. That such a mechanism is operative for the complexes studied here is not surprising. The acetonitrile complex has no remote substituent for attachment of the reductant and must, therefore, proceed by a non-bridged-outer-sphere mechanism. On the other hand, while the cyanoacetamide, succinonitrile and methylcyanoacetate complexes do have additional

Table 8

Summary of Kinetic Parameters for the Reduction of Nitrile Complexes of Pentaamminecobalt(III) by Chromium(II).

Nitrile Ligand	$10^2 \times k(25°)$,[a] $M^{-1}\ s^{-1}$	$\Delta H^{\dagger}$, kcal mol^{-1}	$\Delta S^{\dagger}$, cal mol^{-1} deg^{-1}
$NCCH_3$	0.94(2.0)[b]	10.2±0.4	-33.1±1.4
$NC(CH_2)_2CN$	2.54	9.5±0.4	-34.1±1.1
$NCCH_2CONH_2$	2.61(5.3)[e]	9.0±0.6	-35.6±1.9
$NCCH_2CO_2CH_3$	2.34	9.5±0.5	-34.2±1.3
$NCCH_2CO_2^-$	211	12.5±1.1	-15.2±3.6
$NCCH_2CN$	6.29	-	-
$NCC\overset{-}{H}CN$	700	-	-
Cinnamonitrile[c]	2.2	8.8±0.9	-37±3
Furanacrylonitrile[c]	2.0	9.5±0.8	-34±4
4-Acetoxybenzonitrile[c]	2.1	9.1±1.2	-36±4
Benzonitrile[d]	4.27	-	-

[a] Values in 0.50 M $LiClO_4$-$HClO_4$ unless otherwise noted.

[b] Measured in 0.10 M $HClO_4$-0.90 M $LiClO_4$ at 25°; value agrees with that in 1.0 M $HClO_4$ reported by Hua, L.H.-C.; Balahura, R.J.; Fanchiang, Y.-T.; Gould, E.S. Inorg. Chem. 1978, 17, 3692.

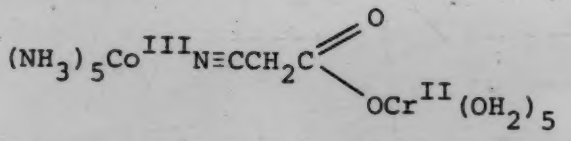
[c] Purcell, W.L.; Balahura, R.J. J. Am. Chem. Soc., 1976, 98, 4457.

[d] In 1.0 M $HClO_4$, Balahura, R.J.; Wright, G.B.; Jordan, R.B., J. Am. Chem. Soc., 1973, 95, 1137.

[e] Measured in ionic strength 1.0 M ($HClO_4$-$LiClO_4$).

functional groups capable of serving as binding sites for chromium(II), they do not have an inner-sphere pathway available. The presence of a saturated methylene group in the ligand destroys the conjugation between reductant and oxidant that is necessary for effective mediation of an electron by an inner-sphere process.

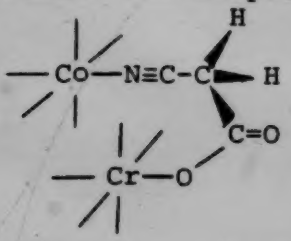
Clearly, the results obtained for the cyanoacetate anion complex are considerably different from those systems just described. The rate constant for reduction is about 100 times larger and the reaction has been shown to proceed with ligand-transfer to chromium(III). These observations imply the formation of a bridged intermediate of the type



$$(NH_3)_5Co^{III}N{\equiv}CCH_2C(=O)OCr^{II}(OH_2)_5 \quad .$$

III-2

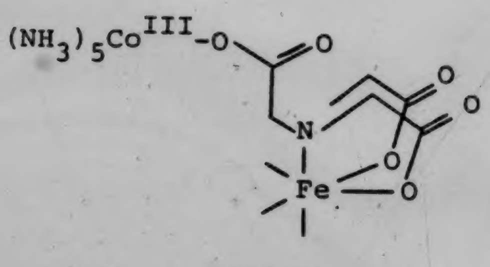
That such an intermediate should provide a facile route for reduction of the cobalt(III) complex is unusual since it would seem to require inner-sphere electron transfer through a saturated ligand. However, this need not be the case since the geometry of the bridged intermediate can be pictured as



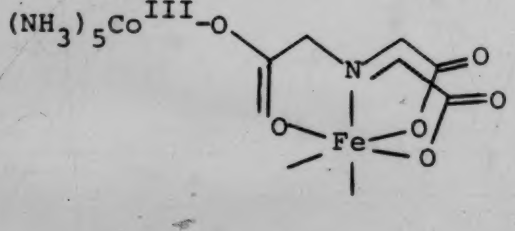
.

This representation shows that the coordination spheres of cobalt(III) and chromium(II) can be brought in close enough contact to facilitate direct electron transfer between the metal centres by an essentially outer-sphere mechanism. This is an example of electron transfer proceeding by a bridged-outer-sphere mechanism.

Although the possibility of such a mechanism for reduction has been recognized for some time, the number of systems thought to proceed by this route are relatively few. Unfortunately, for many of these systems, the results are inconclusive. For example, in their study of the iron(II) reduction of oxygen-bonded (nitrilotriacetato)pentaamminecobalt(III), Cannon and Gardiner[61] obtained evidence for the formation of a precursor complex III-3 in which electron transfer would proceed by a bridged-outer-sphere mechanism.

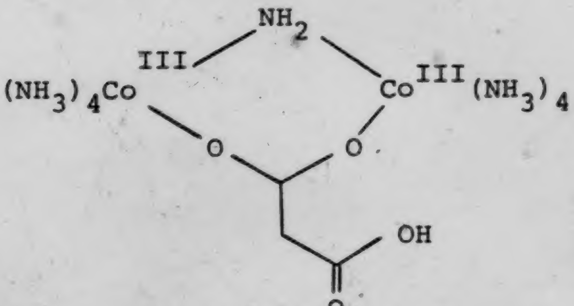


III-3



III-4

However, they were unable to rule out formation of a second intermediate III-4 in which inner-sphere electron transfer via the briding carboxylate could occur. Indirect evidence for a bridged-outer-sphere mechanism was also obtained in the chromium(II) reduction of μ-malonato- and μ-dimethylmalonato-dicobalt(III) complexes of type III-5.[62]



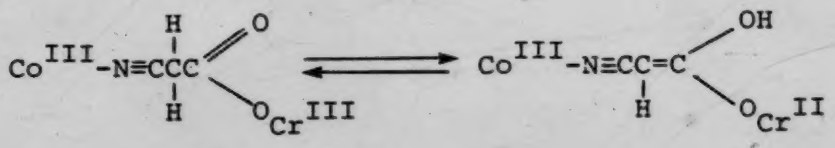
III-5

The reaction pathway with an inverse hydrogen ion dependency was believed to arise from acid dissociation of the remote carboxylate, followed by reductant binding and electron transfer. Isolation of either a binuclear chromium(III)-cobalt(III) product or a dichromium(III) species would have been evidence for a bridged-outer-sphere mechanism. Unfortunately, only mononuclear chromium(III) products were isolated. Presumably, reduction of the second cobalt(III) centre is faster than the first and any dichromium(III) species that may be formed decomposes before the products of reaction are isolated.

A particularly significant example of bridged-outer-sphere electron transfer was demonstrated in the study of the chromium(II) reduction of $(NH_3)_5CoNH_2CH_2CO_2^{2+}$ and the analogous β-alanine complex.[29] Sykes et al.[29] found that ligand-transfer to chromium(III) occurred for both complexes and observed a rate constant of 2.5 M^{-1} s^{-1} for reduction of the glycine anion complex, a value that is very similar to that found in the cyanoacetate system (2.1 M^{-1} s^{-1}). However, contrary to their assertions, the reported electronic spectrum of the chromium(III) product, with maxima at 402 and 560 nm, does not correspond to that of $(H_2O)_5CrO_2CCH_2NH_3^{3+}$ which has maxima at 411-412 and 572-574 nm.[63,64] The product analysis experiment described by Sykes et al,[29] has been repeated, and a product with an extinction coefficient of 20.6 M^{-1} cm^{-1} at both 410 and 574 nm was obtained, in good agreement with the electronic spectrum of $(H_2O)_5CrO_2CCH_2NH_3^{3+}$.[63,64] While the discrepancy in Sykes' characterization of the reduction product has not been accounted for, the subsequent experiments do substantiate Sykes' conclusion that ligand-transfer to chromium(III) occurs in the glycine system, and as such, a bridged-outer-sphere mechanism is operative.

The observation that a bridged-outer-sphere mechanism is operative in the glycine and cyanoacetate systems and not in the closely related cyanoacetamide, methylcyanoacetate and succinonitrile complexes leads to the conclusion that complex formation of chromium(II) at the available binding sites for the latter series is not as favourable as in the former. This probably arises from the lower basicity of these remote functional groups compared to carboxylate. The higher charge of the complexes in this series (3+ as compared to 2+) would also hinder complex formation with chromium(II). In addition, the succinonitrile complex possesses a longer chain of atoms which can adopt a greater number of orientations that are unfavourable for bridged-outer-sphere electron transfer. This would result in a lower probability of reduction proceeding by this mechanism.

While the bridged-outer-sphere mechanism seems to be the simplest way to account for the observations with the cyanoacetate and glycine complexes of pentaamminecobalt(III), the active methylene group in the former[50,60] presents an alternative explanation via the tautomeric equilibrium



III-6 III-7

The transfer of a proton from the methylene group to the carboxylate oxygen yields structure III-7 which has a conjugated system between the metal centers. Electron transfer through the organic ligand by an inner-sphere mechanism then could occur. If the reduction of the cyanoacetate complex did proceed in this manner, then it could be argued that ligand transfer is not observed for the ester complex because the oxygen atoms in the enol form are not sufficiently basic to coordinate to chromium(II). Similarly, ligand-transfer product would not be observed from reduction of the cyanoacetamide complex because the expected proton transfer to oxygen[65] would leave the chromium(II) on the amide nitrogen not in conjugation with cobalt(III). However, such tautomerism does not account for the observations with the glycine complex. Glycine lacks sufficiently activating organic groups to cause such tautomerism, and even if the tautomerism did occur, it would not provide a conjugated pathway between the metal centers because of the presence of the saturated NH_2 group. In view of the great kinetic similarity of the glycine and cyanoacetate systems, the bridged-outer-sphere mechanism is the best way to rationalize the results.

The activation parameters for the chromium(II) reduction of the cyanoacetate anion complex are given in Table 8. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are significantly different from other entries in the table and may in themselves illustrate that a different mechanism is operative for this system. As a result, the 3 kcal mol^{-1} higher $\Delta H^{\ddagger}$ may simply reflect the additional requirement of twisting the ligand-chromium(II) system to within the outer-sphere interaction distance of cobalt(III). Taube *et al.*[66] have suggested that the very negative values of $\Delta S^{\ddagger}$ found for 3+, 2+ charge type reactions (ca. -30 cal mol^{-1} deg^{-1}) is largely due to concentrating the charge in the dielectric medium. As a result, the more positive $\Delta S^{\ddagger}$ found for the cyanoacetate anion complex may arise from its lower formal charge (2+) as compared to the other nitrile complexes in this series (3+). Indeed, since the source of this lower formal charge is the bridging group itself, the observed decrease of ca. 15-20 cal mol^{-1} deg^{-1} would not be unexpected.[67] Unfortunately, activation parameters have not been determined for analogous systems employing a bridged-outer-sphere mechanism for reduction. Until such time that this is done, the reasoning presented for these values remains speculative.

An earlier report by Jordan et al.[68] on the reaction of chromium(II) with the malononitrile complex of $(NH_3)_5Co^{3+}$ indicated that the reaction was very rapid ($k > 400$ M^{-1} s^{-1}). The preliminary results presented here disagree with that report. The rate of reduction of this complex is several orders of magnitude slower than previously reported and exhibits an inverse acid dependence. The acid independent term (0.0629 M^{-1} s^{-1}) is about three times larger than for other nitrile complexes (Table 8) that are believed to undergo non-bridged-outer-sphere reduction. This suggests that the protonated complex is reduced by a bridged-outer-sphere mechanism through an intermediate of the type

$$(NH_3)_5Co^{III}N{\equiv}CCH_2C{\equiv}NCr^{II} \quad .$$

III-8

The absence of a ligand-transfer chromium(III) product seems to argue against the bridged-outer-sphere mechanism. However, as will be discussed in greater detail in Chapters IV and V, many nitrile-bound chromium(III) complexes undergo facile aquation, and the absence of $(H_2O)_5CrNCCH_2CN^{3+}$ in the products does not necessarily constitute evidence against the bridged-outer-sphere mechanism.

If a bridged-outer-sphere mechanism is assumed to be operative in the present system, then a comparison to the cyanoacetate complex is in order. It is interesting to note that the rate constant for reduction of the malononitrile complex is about 30 times smaller than that for the cyanoacetate complex. This is consistent with the higher charge of the former (3+ as compared to 2+) and the lower basicity of the remote nitrile function as compared to the carboxylate group. In addition, molecular models show that the intramolecular distance between the two metal centres in III-8 is greater than for the analogous cyanoacetate system. All of these factors would be expected to reduce the relative reduction rate for the malononitrile complex in a bridged-outer-sphere mechanism.

The inverse acid dependent path for reduction of the malononitrile complex can be rationalized by assuming a bridged-inner-sphere mechanism in which the unprotonated complex is reduced by chromium(II) according to reaction (3.11).

$$\begin{tikzcd}
(NH_3)_5CoNC\overset{-}{C}HCN^{2+} + Cr^{2+} \arrow[r] & {[(NH_3)_5Co^{III}NC\overset{-}{C}HCNCr^{II}]^{\ddagger}} \arrow[d, "H^+"] \\
& 5NH_4^+ + Co^{2+} + (H_2O)_5CrNCCH_2CN^{3+}
\end{tikzcd} \qquad (3.11)$$

As noted earlier, aquation of $(H_2O)_5CrNCCH_2CN^{3+}$ might be expected to be rapid. An inner-sphere mechanism is possible in this case since deprotonation of the methylene carbon provides a conjugated pathway between the oxidant and the reductant on the remote nitrile. The specific rate constant for reduction of the deprotonated complex is rather large (700 $M^{-1}\ s^{-1}$), although not unusually so when compared to the somewhat analogous cyanamide complex $(NH_3)_5CoNCNH^{2+}$ ($3.3 \times 10^3\ M^{-1}\ s^{-1}$).[28]

The inverse acid dependent path could result from attack of chromium(II) at the deprotonated methylene carbon to yield the organochromium product III-9.

$$(H_2O)_5CrCH(CN)_2^{\ 2+}$$

III-9

However, species III-9 might have been expected to be sufficiently stable to be detected in the product analysis study.[33-37] No such species was observed.

The second reaction observed during the reduction of the malononitrile complex has been attributed to the reaction of chromium(II) with the carboxamide complex $(NH_3)_5CoNHC(O)CH_2CN^{2+}$. Little can be said about the mechanism of reduction for this complex since the appropriate product studies were not undertaken. Based on the results obtained for other carboxamide complexes,[27,69] it is possible that reduction proceeds by attack of chromium(II) on the carboxamide oxygen by a bridged-inner-sphere mechanism. It is interesting to note that the rate constant for reduction of $(NH_3)_5CoNHC(O)CH_2CN^{2+}$ (1.0×10^{-2} M^{-1} s^{-1}) is similar to that for the 3-carboxamidopyridine complex (1.65×10^{-2} M^{-1} s^{-1}) for which inner-sphere reduction was proposed.[69]

CHAPTER IV

Organochromium(III) Complexes of Acetonitrile.

Introduction

The first aquoorganochromium(III) species containing a chromium-carbon σ bond was the complex $(H_2O)_5CrCH_2C_6H_5^{2+}$ isolated by Anet and Leblanc.[70] Since this first work, a great number of similar organochromium(III) compounds have been prepared[33-35,37,71-74] and their reactivity with other reagents investigated.[75-79] Although organochromium(III) species have been prepared in a variety of ways,[37,80-83] one of the simplest procedures involves the reaction of alkyl halides with chromium(II):

$$\begin{aligned} RCH_2X + Cr^{2+} &\longrightarrow RCH_2\cdot + (H_2O)_5CrX^{2+} \\ RCH_2\cdot + Cr^{2+} &\longrightarrow (H_2O)_5CrCH_2R^{2+} \end{aligned} \qquad (4.1)$$

The $RCH_2\cdot$ radical generated via halogen abstraction by chromium(II) can react with a second equivalent of chromium(II) to yield the organochromium(III) complex.

In the present study, the reactions of chromium(II) with chloro- and iodo-substituted acetonitrile have been investigated. In addition, the reactions of chromium(II) with the $(NH_3)_5Co^{3+}$ complexes of these ligands have been studied to determine what influence a coordinated, oxidizing metal centre has on the reactions of the ligand.

Experimental

The syntheses of the pentaamminecobalt(III) complexes of chloroacetonitrile and iodoacetonitrile have been described in Chapter II.

Product Analysis

Products of reaction were determined by charging reaction mixtures onto columns of Dowex 50W-X2 or Sephadex SP-C25 cation-exchange resin. Elution was achieved using increasingly concentrated solutions of perchloric acid. For those systems in which the isolated complexes were required for subsequent kinetic studies, the cobalt and/or chromium content of the fraction was determined as described in Chapter II. The acid concentration of the fraction was determined by passing an aliquot of the solution through a column of Dowex 50W-X8 cation-exchange resin that was in the H^+ form and titrating the liberated acid with standard NaOH. A small correction to the acidity was made for the known concentration of the complex in solution.

In order to ascertain the organic products of the reaction of $NCCH_2I$ with chromium(II), reaction mixtures were analyzed by ^{13}C NMR spectroscopy. After the reaction had proceeded for 10 half-times, the reaction mixtures were air-oxidized. The resulting solutions were distilled and any volatile organic products were co-distilled with the water, leaving behind any chromium(III) products. Distillations were done at both atmospheric pressures and at 0.3 torr. Solutions of the distillate in 10% D_2O were prepared using $(CH_3)_3COH$ as an internal standard, and the ^{13}C NMR spectra were recorded.

Kinetic Measurements

All reactions were studied under pseudo-first-order conditions and, except for those systems listed below, all exhibited monophasic behaviour.

The reaction of $NCCH_2Cl$ with chromium(II) showed biphasic kinetic behaviour throughout the electronic spectrum. The largest absorbance changes in the visible region were observed near 428 and 609 nm, wavelengths which are characteristic of $(H_2O)_5CrCl^{2+}$.[84] Complications arose in trying to fit the absorbance data at 428 nm since both $(H_2O)_5CrCl^{2+}$ and $(H_2O)_5CrCH_2CN^{2+}$, which is also formed in the reaction, absorb at this wavelength and both react with excess chromium(II) at different specific rates. At 609 nm, only $(H_2O)_5CrCl^{2+}$ absorbs and from independent studies it was determined that the second reaction observed in the reduction of $NCCH_2Cl$ corresponded to chromium(II) catalyzed aquation of $(H_2O)_5CrCl^{2+}$ for which the rate law is of the form

$$\frac{-d[(H_2O)_5CrCl^{2+}]}{dt} = \frac{k_2[(H_2O)_5CrCl^{2+}][Cr^{2+}]}{[H^+]} \qquad (4.2)$$

The value of k_2 was determined to be $(2.29 \pm 0.07) \times 10^{-4}$ s^{-1} (25°C, 0.50 M $LiClO_4$-$HClO_4$), in good agreement with previous reports,[85,86] considering the different reaction conditions. Absorbance-time curves for the reaction of $NCCH_2Cl$ with chromium(II) were obtained at 609 nm and subjected to non-linear least-squares fitting to the scheme

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \quad . \qquad (4.3)$$

With k_2 held constant at the value given above, acceptable values for k_1 were obtained.

The reaction of $(NH_3)_5CoNCCH_2Cl^{3+}$ with chromium(II) was even more complicated. Data collected at 609 nm were fitted by scheme (4.3) while data collected at 417 nm were fitted best by the scheme

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \quad . \qquad (4.4)$$

The equations for both schemes are described in Appendix A. Data was collected for only as long as required to obtain a good fit for the first reaction. No effort was made to systematically determine the rate laws for the subsequent reactions.

Results

$NCCH_2I + Cr^{2+}$.

The stoichiometry of the reaction of chromium(II) with iodoacetonitrile was determined by analyzing for the chromium(II) remaining after ten half-times. The analysis was carried out by oxidation of the remaining chromium(II) with excess iron(III) and determining the excess iron(III) iodometrically. The stoichiometry of the reaction was found to be 2.09 ± 0.01 Cr(II): 1.00 $NCCH_2I$.

Chromatographic separation of reaction mixtures of $NCCH_2I$ and chromium(II) on Dowex 50W-X2 showed that in addition to $Cr(OH_2)_6^{3+}$, two other chromium(III) complexes were formed. The first species is assigned as $(H_2O)_5CrI^{2+}$, on the basis of its elution properties, its electronic spectrum,[84] and its hydrolytic instability.[84] Presumably, it is formed by the halogen abstraction reaction

$$NCCH_2I + Cr^{2+} \longrightarrow NCCH_2\cdot + (H_2O)_5CrI^{2+} \quad . \qquad (4.5)$$

The second chromium(III) species isolated is a red product which elutes as a dipositive ion and is remarkably inert to hydrolysis. No decomposition is observed over a period of several weeks at 5°C. The electronic spectrum of this species exhibits maxima at 527, 409, 262 and 209 nm with extinction coefficients of 40.3, 102, 4430 and 6460 M^{-1} cm^{-1}, respectively. The band maxima are characteristic of an organochromium(III) species and the complex is formulated as

$$(H_2O)_5CrCH_2CN^{2+} \quad .$$

IV-1

Its formation can be attributed to the reaction of a second chromium(II) with the generated acetonitrile radical .

$$NCCH_2\cdot + Cr^{2+} \longrightarrow (H_2O)_5CrCH_2CN^{2+} \quad . \qquad (4.6)$$

Funke and Espenson[87] have reported the preparation of complex IV-1 using a different synthetic procedure. However, the reported extinction coefficients are ca. 35% lower than found in this study. In light of the very poor yield reported by Funke and Espenson,[87] it is likely that their sample was contaminated with $Cr(OH_2)_6{}^{3+}$.

The relative yields of $(H_2O)_5CrCH_2CN^{2+}$ as a function of ligand concentration are shown in Table 9. It is worth noting that the same quantity of the organochromium(III) species is obtained regardless of whether $NCCH_2I$ or chromium(II) is in excess. Nevertheless, 75% of the reaction yields products other than $(H_2O)_5CrCH_2CN^{2+}$. Since the only chromium-containing products of the reaction are $(H_2O)_5CrCH_2CN^{2+}$, $(H_2O)_5CrI^{2+}$ and $Cr(OH_2)_6{}^{3+}$, the unaccounted for products must be strictly organic in nature.

Table 9

Ion-Exchange Analysis of $(H_2O)_5CrCH_2CN^{2+}$ Formed from the Reaction of $NCCH_2I$ with Chromium(II).

10^2x[$NCCH_2I$], M	10^2x[Cr(II)], M	[H^+], M	$(H_2O)_5CrCH_2CN^{2+}$ [a] %
3.45	9.28	0.100	25.0[b]
6.90	9.28	0.100	24.5[c]

[a] Determined as chromate.

[b] Based on total number of moles of $NCCH_2I$.

[c] Based on half the number of moles of chromium(II).

In order to determine these organic products, ^{13}C NMR spectroscopy was employed. Solutions were prepared as described in the Experimental Section and the sole organic product detected was acetonitrile. This may imply that the acetonitrile radical intermediate can also react with excess chromium(II) to ultimately generate free acetonitrile.

$$NCCH_2\cdot + Cr^{2+} \xrightarrow[H^+]{} NCCH_3 + Cr(OH_2)_6^{3+} \qquad (4.7)$$

This would account for the substantial amounts of $Cr(OH_2)_6^{3+}$ observed during the ion-exchange procedure.

The kinetics of the reaction of iodoacetonitrile with chromium(II) were studied at 528 nm and the reaction was found to obey the rate law

$$\frac{d[(H_2O)_5CrCH_2CN^{2+}]}{dt} = k[NCCH_2I][Cr^{2+}] \quad . \qquad (4.8)$$

The rate data are summarized in Table C-5 of Appendix C. The rate constants and activation parameters are given in Table 10.

$NCCH_2Cl + Cr^{2+}$.

The reaction of chloroacetonitrile with chromium(II) is qualitatively different from that just described for iodoacetonitrile. The reaction is much slower and exhibits

Table 10

Kinetic Parameters for the Chromium(II) Reduction of $NCCH_2I^a$

Temp., °C	k, $M^{-1}\ s^{-1}$	$\Delta H^{\dagger}$, kcal mol^{-1}	$\Delta S^{\dagger}$, cal mol^{-1} deg^{-1}
15.3	6.76±0.23		
25.0	9.17±0.41	5.44±0.74	-35.8±2.5
35.0	13.3±0.7		

[a] Ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Errors quoted are 95% confidence limits.

biphasic kinetic behaviour. Scan runs indicated that the first reaction produced $(H_2O)_5CrCl^{2+}$ which underwent chromium(II) catalyzed aquation[85] in the second reaction. Employing the data-fitting procedure described in the Experimental Section, it was found that the first reaction followed the rate law

$$\frac{d[(H_2O)_5CrCl^{2+}]}{dt} = k_1[NCCH_2Cl][Cr^{2+}] \quad . \qquad (4.9)$$

The rate data are summarized in Table C-6 of Appendix C. The value of k_1 was found to be $(1.07 \pm 0.07) \times 10^{-2}$ M^{-1} s^{-1} (25°C, 0.50 M $LiClO_4$-$HClO_4$).

Although detailed product studies were not undertaken for this system, ion-exchange experiments indicated that there was extensive formation of $(H_2O)_5CrCl^{2+}$ and $Cr(OH_2)_6{}^{3+}$. Although a distinct band corresponding to $(H_2O)_5CrCH_2CN^{2+}$ could not be isolated, later fractions of the $(H_2O)_5CrCl^{2+}$ band indicated that some of the former was present. It was estimated that 5-10% $(H_2O)_5CrCH_2CN^{2+}$ was detected in this manner, a value that is in agreement with scan runs of the reduction which showed that the absorbance in the 410-430 nm region was higher than could be accounted for if only $(H_2O)_5CrCl^{2+}$ and $Cr(OH_2)_6{}^{3+}$ were formed in the reaction.

$\underline{(H_2O)_5CrCH_2CN^{2+} + Cr^{2+}}$.

The reduction of this organochromium(III) species was found to be first-order in both $(H_2O)_5CrCH_2CN^{2+}$ and chromium(II). However, upon varying the acid concentration (0.393 to 0.050 M), it was observed that the second-order rate constant (k_{obsd}) increases with decreasing $[H^+]$. A plot of k_{obsd} vs. $[H^+]^{-1}$ is linear, as shown in Figure 3, and is consistent with a rate law of the form

$$k_{obsd} = a + \frac{b}{[H^+]} \tag{4.10}$$

Table C-7 of Appendix C gives a summary of the rate data obtained. The simplest mechanism consistent with the experimental rate law is

$$\begin{tikzcd}
(H_2O)_5CrCH_2CN^{2+} \arrow[rr, shift left, "K_a"] \arrow[dr, "k_1"', "Cr^{2+}"] & & (H_2O)_4(HO)CrCH_2CN^{+} + H^{+} \arrow[ll, shift left] \arrow[dl, "k_2", "Cr^{2+}"'] \\
& \text{Products} &
\end{tikzcd} \tag{4.11}$$

This proposed scheme yields a rate law of the form

$$k_{obsd} = \frac{k_1[H^+] + k_2K_a}{K_a + [H^+]} \tag{4.12}$$

If it is assumed that $K_a << [H^+]$, then equation (4.12) simplifies to

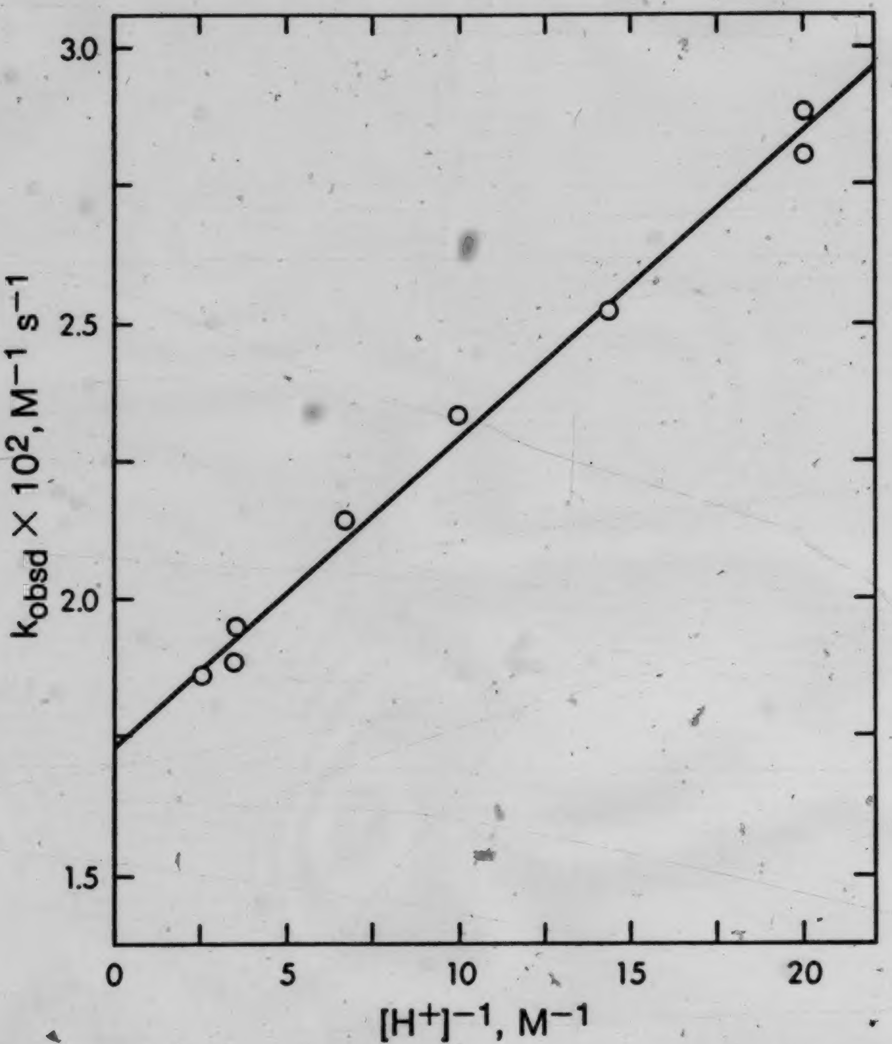


FIGURE 3. Variation of k_{obsd} with $[H^+]^{-1}$ for the reduction of $(H_2O)_5CrCH_2CN^{2+}$ by Cr^{2+} at 25°C in 0.50 M $LiClO_4$-$HClO_4$.

$$k_{obsd} = k_1 + \frac{k_2K_a}{[H^+]} \qquad (4.13)$$

which has the same form as that obtained experimentally (equation (4.10)). The calculated values of k_1 and k_2K_a were found to be (1.73 ± 0.07) x 10^{-2} M^{-1} s^{-1} and (5.62 ± 0.70) x 10^{-4} s^{-1}, respectively (25°C, 0.50 M $LiClO_4$-$HClO_4$).

Scan runs of reaction mixtures at various acidities showed that $Cr(OH_2)_6^{3+}$ was the sole product of reaction, and not some more strongly absorbing species.

$\underline{(H_2O)_5CrCH_2CN^{2+} + Hg^{2+}}$.

The reaction of mercury(II) with $(H_2O)_5CrCH_2CN^{2+}$ was re-examined and compared to the results obtained by Funke and Espenson.[87] In agreement with that report, absorbance changes at 409 nm were found to correspond to the rate law

$$\frac{-d[(H_2O)_5CrCH_2CN^{2+}]}{dt} = k[(H_2O)_5CrCH_2CN^{2+}][Hg^{2+}] \cdot \qquad (4.14)$$

The rate data are summarized in Table C-8 of Appendix C. The second-order rate constant was found to be 8.7 ± 0.4 M^{-1} s^{-1} (25°C, 1.00 M $LiClO_4$-$HClO_4$). This value is in reasonable agreement with the value 9.8 ± 0.3 M^{-1} s^{-1}

(25°C, 1.00 M $HClO_4$) which was reported previously by Funke and Espenson.[87]

The visible spectra of reactant solutions at the completion of reaction were consistent with $Cr(OH_2)_6^{3+}$ as the chromium(III) product. No effort was made to ascertain the nature of the mercury(II) product. However, by comparison to analogous systems,[79] the product is expected to be $HgCH_2CN^+$.

$\underline{(NH_3)_5CoNCCH_2I^{3+} + Cr^{2+}}$.

The stoichiometry of the reaction of chromium(II) with the iodoacetonitrile complex of $(NH_3)_5Co^{3+}$ was determined in a manner analogous to that described earlier for free iodoacetonitrile ligand. The results obtained indicated that the stoichiometry was 2.03 ± 0.02 Cr(II): 1.00 $(NH_3)_5CoNCCH_2I^{3+}$.

Preliminary product studies revealed that two major chromium(III) species were formed. Rapid elution of reaction mixtures on Dowex 50W-X2 resin revealed the production of a green, dipositive species whose electronic spectrum corresponded to that of $(H_2O)_5CrI^{2+}$.[84] The second product was a highly-charged red species which did not move down the column even when eluting with a solution of 0.5 M $HClO_4$ in 1.0 M $NaClO_4$.

The nature of this highly-charged species was elucidated by using Sephadex SP-C25 cation-exchange resin.

After allowing the reaction to proceed to completion, the reaction mixture was air-oxidized, the solution diluted and then allowed to stand for thirty minutes. During this time, aquation of $(H_2O)_5CrI^{2+}$ to $Cr(OH_2)_6^{3+}$ and I^- would be complete.[84] The solution was charged onto the column of resin and elution of the various bands achieved using increasingly concentrated solutions of $NaClO_4$ and $HClO_4$. The results obtained are summarized in Table 11.

Essentially quantitative recovery of I^- was observed. This implies that the halogen transfer reaction (4.15)

$$(NH_3)_5CoNCCH_2I^{3+} + Cr^{2+} \longrightarrow (NH_3)_5CoNCCH_2\cdot^{3+} + (H_2O)_5CrI^{2+} \qquad (4.15)$$

is complete. The observation that no Co^{2+} is formed during the reaction of the iodoacetonitrile complex with chromium(II) indicates that electron transfer reactions involving the cobalt(III) center do not occur in either the original complex or any generated intermediate. Therefore, reactions such as outer-sphere reduction of $(NH_3)_5CoNCCH_2I^{3+}$

$$(NH_3)CoNCCH_2I^{3+} + Cr^{2+} \longrightarrow Co^{2+} + 5NH_3 + Cr(OH_2)_6^{3+} + NCCH_2I \qquad (4.16)$$

and intramolecular electron transfer of the radical intermediate

Table 11

Ion-Exchange Analysis of the Reaction of $(NH_3)_5CoNCCH_2I^{3+}$ with Chromium(II)

Reactant Concentration, M			Product Distribution, %[a]				
$10^3 x [Co^{III}]$	$10^2 x [Cr(II)]$	$[H^+]$	I^- [b]	Co^{2+} [c]	$Cr(OH_2)_6^{3+}$ [d]	$(NH_3)_5CoNCCH_3^{3+}$ [c]	$(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ [c,d]
8.85	2.15	0.101	99.3	0	117	<5	95.2

[a] Based on total number of moles of cobalt(III) complex.

[b] Determined by Volhardt titration.

[c] Cobalt products were determined by conversion to $Co(SCN)_4^{2-}$.

[d] Chromium(III) product was determined by ion-exchange separation and oxidation to CrO_4^{2-}.

$$(NH_3)_5CoNCCH_2\cdot^{3+} \longrightarrow Co^{2+} + 5NH_3 + NCCH_2^{+} \qquad (4.17)$$

$$NCCH_2^{+} \xrightarrow{H_2O} NCCH_2OH + H^{+}$$

are not observed.

A small amount of a yellow complex, which eluted as a tripositive ion, was also observed. Although this species could not be cleanly separated from $Cr(OH_2)_6^{3+}$, analysis of this fraction showed that it contained cobalt to an extent of ca. 5% of that originally present. On the basis of its elution behaviour and colour, this product is assumed to be $(NH_3)_5CoNCCH_3^{3+}$, although it must be emphasized that this assignment is speculative. Its formation could arise from the reaction

$$(NH_3)_5CoNCCH_2\cdot^{3+} + Cr^{2+} \xrightarrow{H^+} (NH_3)_5CoNCCH_3^{3+} + Cr(OH_2)_6^{3+} \qquad (4.18)$$

Such a reaction could be regarded as an outer-sphere electron transfer reaction between chromium(II) and the acetonitrile complex intermediate. Such a reaction would help to explain the relatively high recovery of $Cr(OH_2)_6^{3+}$. The latter is also formed from the aquation of $(H_2O)_5CrI^{2+}$ and from air-oxidation of excess chromium(II).[88]

The highly-charged red species was eluted from the column with 1.0 M $HClO_4$ and was found to account for essentially all of the cobalt initially present. In addition, the chromium content of this band was determined and the ratio of cobalt to chromium was found to be 1.00:1.01. The electronic spectrum of this species was recorded and is shown in Figure 4. The absorption maxima are located at 477, 417 and 256 nm with extinction coefficients of 103, 102 and 6800 M^{-1} cm^{-1}, respectively. Also shown in Figure 4 is the spectrum of $(H_2O)_5CrCH_2CN^{2+}$. It is interesting to note that both complexes have maxima near 260 nm and in the 410-420 nm region. In addition, the band at 477 nm observed for the cobalt-containing species is suggestive of a nitrile complex of $(NH_3)_5Co^{3+}$. These observations coupled with its elution behaviour lead to the formulation of the complex as

$$(NH_3)_5CoN{\equiv}CCH_2Cr(OH_2)_5^{5+} \quad .$$

IV-2

Complex IV-2 is formed presumably by reaction of the radical intermediate with a second equivalent of chromium(II) according to the reaction

$$(NH_3)_5CoN{\equiv}CCH_2\cdot^{3+} + Cr^{2+} \longrightarrow (NH_3)_5CoN{\equiv}CCH_2Cr(OH_2)_5^{5+} \quad . \tag{4.19}$$

It is worth noting that complex IV-2 exhibits remarkable stability in solution. No decomposition of the complex is observed in 0.5 M $HClO_4$ after several months at 5°C.

The kinetics of the formation of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ from the iodoacetonitrile complex and chromium(II) were

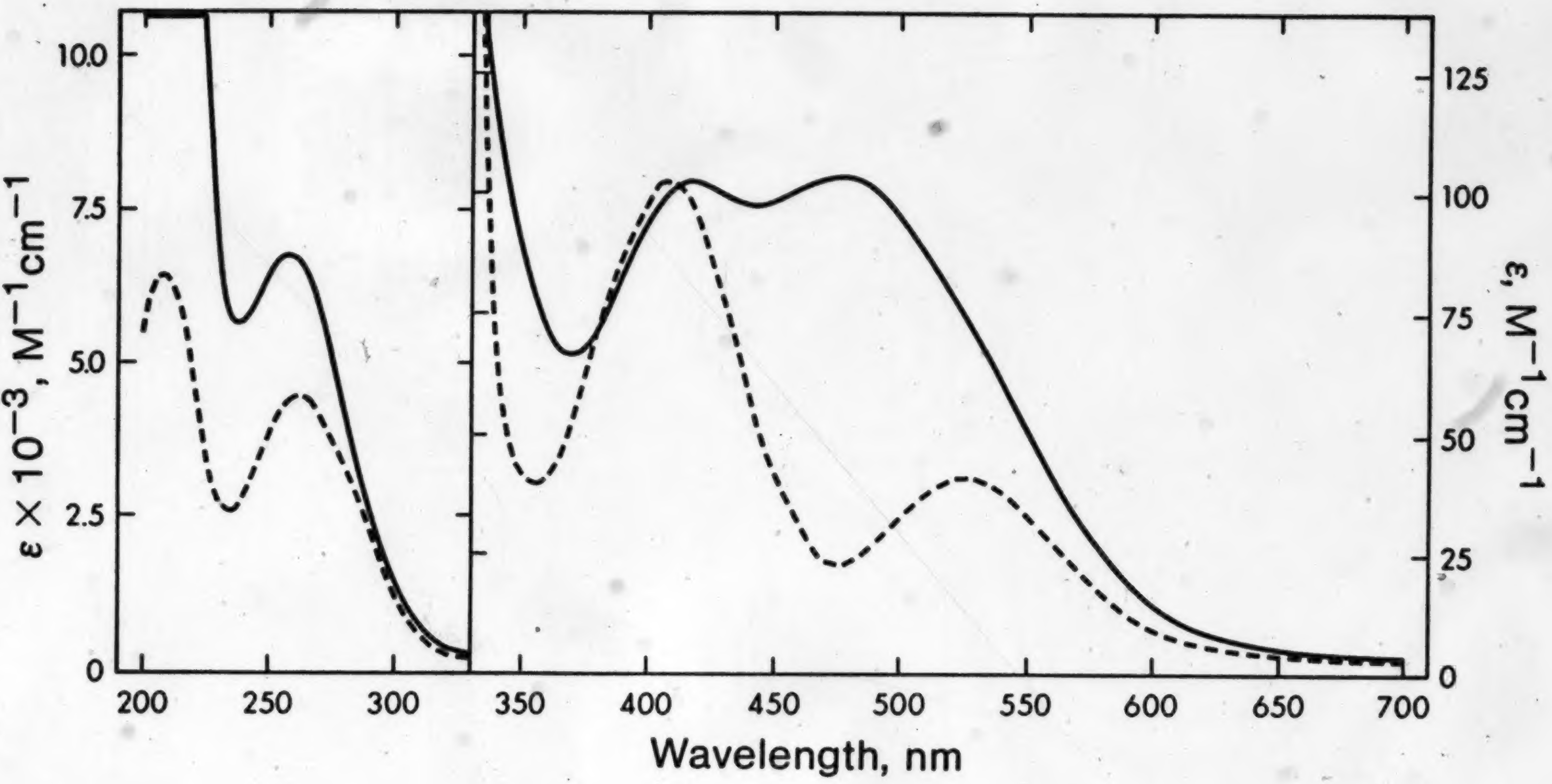


FIGURE 4. Electronic absorption spectra of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ (——) and $(H_2O)_5CrCH_2CN^{2+}$ (----) at 25°C in 0.50 M $HClO_4$.

studied at 477 and 650 nm. The reaction was found to be first order in both the cobalt(III) complex and chromium(II), and obeyed the rate law

$$\frac{d[\text{IV-2}]}{dt} = k[(NH_3)_5CoNCCH_2I^{3+}][Cr^{2+}] \quad . \qquad (4.20)$$

The experimental rate data are summarized in Table C-9 of Appendix C. The rate constants and activation parameters for this reaction are listed in Table 12.

$\underline{(NH_3)_5CoNCCH_2Cl^{3+} + Cr^{2+}}$.

The reaction of the chloroacetonitrile complex with chromium(II) was also studied to ascertain whether it behaves the same as the iodoacetonitrile complex. Product analysis experiments revealed that quite different results are obtained. Because the rate of reduction of this complex is much slower than that for the iodoacetonitrile complex, reaction mixtures were allowed to proceed for only 3-4 half-times. This was necessary since it was found that $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, which is a product of the reaction, also reacts with chromium(II) over longer reaction times. In addition to the unreacted chloroacetonitrile complex and $(H_2O)_5CrCl^{2+}$, which results from the halogen transfer reaction to chromium(III), two cobalt-containing products were observed, Co^{2+} and $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$. The reaction conditions and

Table 12

Kinetic Parameters for the Reaction of $(NH_3)_5CoNCCH_2I^{3+}$ with Chromium(II)[a]

Temp., °C	k, $M^{-1}\ s^{-1}$	$\Delta H^{\dagger}$, kcal mol^{-1}	$\Delta S^{\dagger}$, cal mol^{-1} deg^{-1}
15.3	35.8±1.1		
25.0	45.2±1.6	3.80±0.55	−38.2±1.9
34.4	60.5±0.7		

[a] Ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Errors quoted are 95% confidence limits.

relative distributions of the cobalt products are given in Table 13. The percentages cited are based on the assumption that no $(NH_3)_5CoNCCH_3^{3+}$ is formed in the reaction. In light of the results previously discussed for the iodoacetonitrile complex, such an assumption should yield an error of at most a few percent.

The results show that, unlike the iodoacetonitrile complex, Co^{2+} is formed during the reduction of $(NH_3)_5CoNCCH_2Cl^{3+}$. In fact, this reaction now constitutes more than half of the total reaction. This probably arises from the outer-sphere reduction of the chloroacetonitrile complex

$$(NH_3)_5CoNCCH_2Cl^{3+} + Cr^{2+} \longrightarrow Co^{2+} + 5NH_3 + NCCH_2Cl + Cr(OH_2)_6^{3+} \quad . \tag{4.21}$$

This reaction also accounts for the $Cr(OH_2)_6^{3+}$ product of the reaction. Subsequent kinetic studies confirm that chlorine abstraction is likely to be competitive with outer-sphere reduction. The outer-sphere reaction is not observed with the iodoacetonitrile complex because halogen abstraction is over 500 times faster than with the chloroacetonitrile complex.

Attempts were made to study the kinetics of the reaction of chromium(II) with $(NH_3)_5CoNCCH_2Cl^{3+}$. However, since the reaction is so slow, difficulties were encountered

Table 13

Ion-Exchange Analysis of Reaction of $(NH_3)_5CoNCCH_2Cl^{3+}$ with Chromium(II).

Reactant Concentrations, M			Product Distribution, %[a,b]	
$10^3 x[Co(III)]$	$10^2 x[Cr(II)]$	$[H^+]$	Co^{2+}	$(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$
3.29	4.20	0.102	55.1	44.9
3.92	4.10	0.188	53.4	46.6

[a] Based on total number of moles of cobalt(III) complex.

[b] Cobalt complexes were determined by conversion to $Co(SCN)_4^{2-}$.

in analyzing the absorbance changes attributed to this reaction. The reaction to be monitored is competitive with the chromium(II) catalyzed aquation of $(H_2O)_5CrCl^{2+}$ [85] and with the reaction of chromium(II) with $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$. In addition, the reaction of chromium(II) with $NCCH_2Cl$, which is liberated from outer-sphere reduction of the complex, is also competitive with the reaction to be studied. That all these reactions are operative explains the observed wavelength dependency of the absorbance changes. Nevertheless, the reactions were monitored at 609 and 417 nm and analyzed by non-linear least-squares fitting of the absorbance data to 2- and 3-consecutive reaction schemes, respectively. These are described in greater detail in the Experimental Section and Appendix A. The results obtained in this limited study are given in Table C-10 of Appendix C. The initial reaction was found to obey the rate law

$$\frac{d[\mathrm{IV\text{-}2}]}{dt} = k_1[(NH_3)_5CoNCCH_2Cl^{3+}][Cr^{2+}] \quad . \qquad (4.22)$$

This second-order rate constant was determined to be $(8.9 \pm 0.7) \times 10^{-2}\ M^{-1}\ s^{-1}$ (25°C, 0.50 M $LiClO_4$-$HClO_4$). It must be emphasized, however, that this rate constant is only approximate because of the complexity of the system and the simplistic approach taken to analyze it.

$\underline{(NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+} + Cr^{2+}}$.

Shown in Figure 5 are the spectral changes associated with the reaction of $(NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+}$, IV-2, with chromium(II). The reaction gave a monophasic decrease in absorbance at both 417 and 477 nm, and obeyed the rate law

$$\frac{-d[\text{IV-2}]}{dt} = k[\text{IV-2}][Cr^{2+}] \quad . \tag{4.23}$$

The experimental rate data are given in Table C-11 of Appendix C. The rate constant was found to be (2.39 ± 0.10) x 10^{-3} M^{-1} s^{-1} (25°C, 0.50 M $LiClO_4$-$HClO_4$).

Because of the very slow rate of this reaction and the necessity of having large concentrations of chromium(II) present to achieve a reasonably short reaction time, product analysis experiments were not undertaken. However, the relative absorbance changes and the spectrum of the final solution were consistent with $Cr(OH_2)_6{}^{3+}$ as the sole chromium(III) species formed. Tests on reaction mixtures for Co^{2+} were positive.

$\underline{(NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+} + Hg^{2+}}$.

Since mercury(II) is known to react with simple organochromium(III) species to yield organomercurials,[79] studies were undertaken to see if a similar reaction

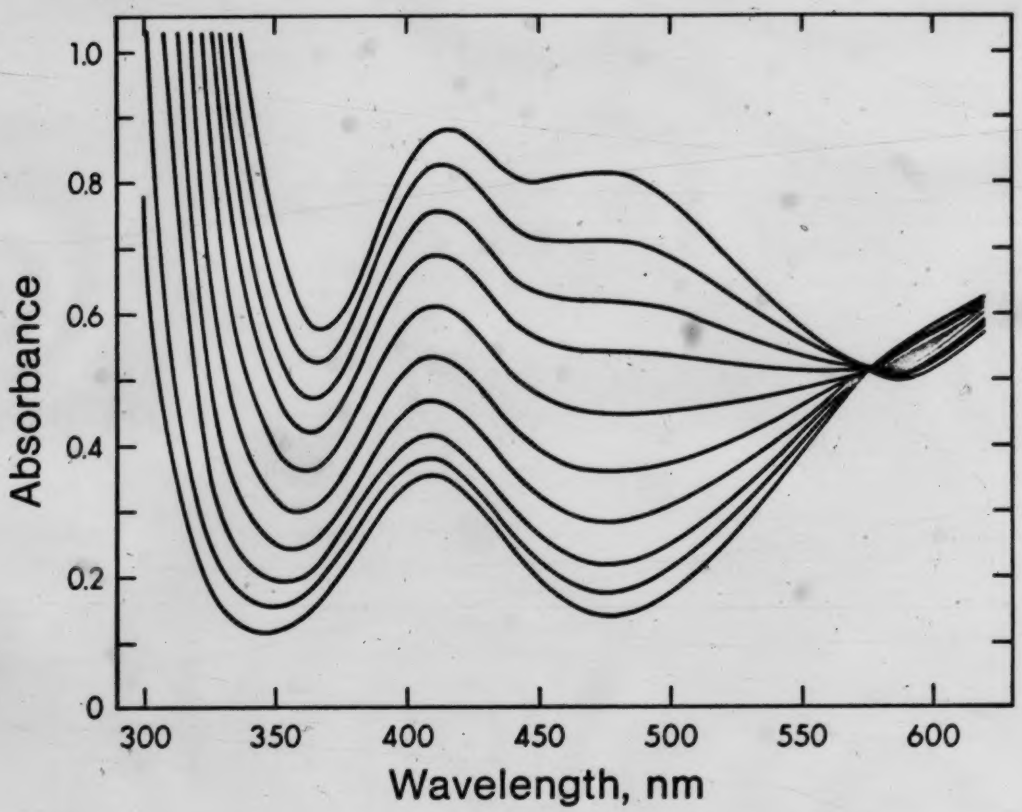


FIGURE 5. Change in visible spectrum during reduction of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ (1.60×10^{-3} M) by chromium(II) (3.13×10^{-2} M); $[H^+] = 0.28$ M; 25°C; Ionic strength 0.50 M ($LiClO_4$); 5 cm cell. The absorbance is decreasing below the isosbestic point at 577 nm. The spectral scans were started at 4, 48, 88, 128, 188, 268, 368, 508, 608 and 1158 minutes after mixing.

occured with $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$. The absorbance changes associated with the reaction are shown in Figure 6. The absorbance maximum at 417 nm, attributed to the organochromium(III) entity is observed to disappear whereas the maximum at 477 nm, although its intensity is decreased and shifts to slightly smaller wavelength, is retained. Therefore, while the organochromium(III) moiety is destroyed, the pentaamminecobalt(III) remains intact.

A product analysis study was undertaken. A solution of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ (5.5×10^{-3} M) in 0.100 M $HClO_4$ was allowed to react for 3.5 h with Hg^{2+} (0.021 M) and then charged onto a column of Sephadex SP-C25 resin. A blue band eluting as a tripositive species was observed and found to be $Cr(OH_2)_6^{3+}$ on the basis of its visible spectrum. A more strongly retained yellow fraction was also observed and was eluted from the resin with 1.0 M $HClO_4$. The cobalt content of this fraction was determined and its electronic spectrum recorded. Maxima were observed at 471 and 335 nm with extinction coefficients of 75.6 and 67.6 M^{-1} cm^{-1}, respectively. These absorption bands occur in regions expected for nitrile complexes of $(NH_3)_5Co^{3+}$. A positive dithizone test for this fraction indicated that the product contained mercury(II).[79,89] Based on these results, the product is formulated as

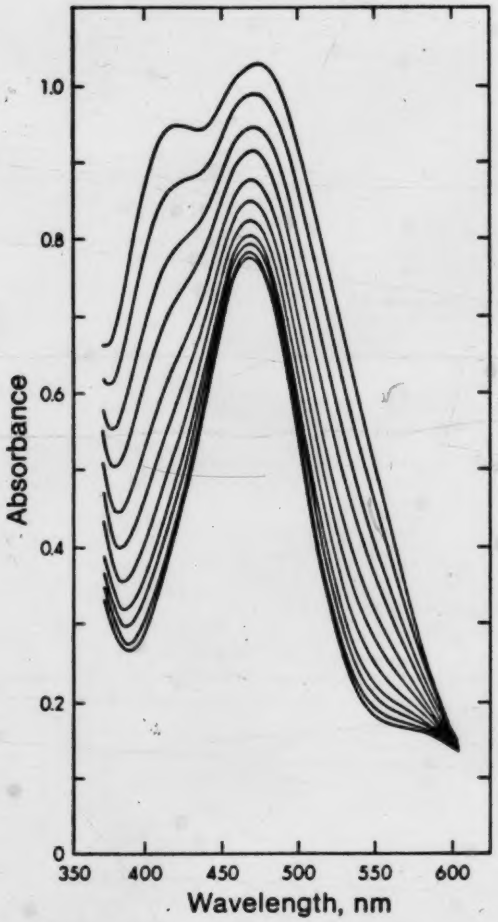


FIGURE 6. Change in visible spectrum during reaction of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ (2.00×10^{-3} M) with mercury(II) (2.01×10^{-2} M); $[H^+] = 0.08$ M; 25°C; Ionic strength 1.00 M ($LiClO_4$); 5 cm cell. The absorbance is decreasing with time. The spectral scan runs were started at 1, 4, 8, 12, 18, 24, 32, 42, 52, 72 and 151 minutes after mixing.

$(NH_3)_5CoN{\equiv}CCH_2Hg(OH_2)^{4+}$

IV-3

Product analysis results indicate that the ratio of the starting material $(NH_3)_5CoNCCH_2Cr(OH_2)_6^{5+}$ to the products $Cr(OH_2)_6^{3+}$ and $(NH_3)_5CoNCCH_2Hg(OH_2)^{4+}$ formed is 1.00:0.99:0.96.

In an effort to more fully confirm the nature of this novel dimetallic organomercury(II) complex, a solid sample of the perchlorate salt of this complex was prepared and characterized by elemental analysis, visible spectrophotometry, and infrared and ^1H NMR spectroscopies. The results are shown in Table 14. Two observations should be noted in particular. A nitrile stretch at 2269 cm^{-1} is observed which indicates that the nitrile function has not undergone hydrolysis to yield the carboxamide complex. The ^1H NMR spectrum clearly demonstrates the presence of cis- and trans-ammines as well as the methylene group. In addition, as shown in Figure 7, coupling between ^{199}Hg ($I = 1/2$) and the methylene protons is observed. This is conclusive evidence that mercury is coordinated to the methylene group and serves to substantiate the formulation of the complex as IV-3.

The kinetics of this reaction of mercury(II) with $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ were studied at 417 nm. The

Table 14

Results of Characterization of $[(NH_3)_5CoNCCH_2Hg(OH_2)](ClO_4)_4$

Elemental Analysis

Anal. Calcd.: Co, 7.36; C, 3.00; H, 2.39; N, 10.50.

Found: Co, 7.31; C, 3.24; H, 2.40; N, 10.66.

Infrared[a]

$\nu(C{\equiv}N)$ 2269(s)

Electronic Spectrum[b]

λ, nm (ε_{max}, M^{-1} cm^{-1})

471(75.6)

335(67.6)

^1H NMR[c]

cis NH_3's, 6.28 τ

trans NH_3, 6.72 τ

$-CH_2-$, 7.49 τ

$J(^{199}Hg-^1H)$, 312 Hz[d]

---

[a] Spectrum obtained in KBr disk.

[b] Recorded in 0.50 M $HClO_4$.

[c] Recorded in Me_2SO-d_6. Shifts are relative to the residual solvent protons at 7.48 τ.

[d] In D_2O, $J(^{199}Hg-^1H)$ is 361 Hz.

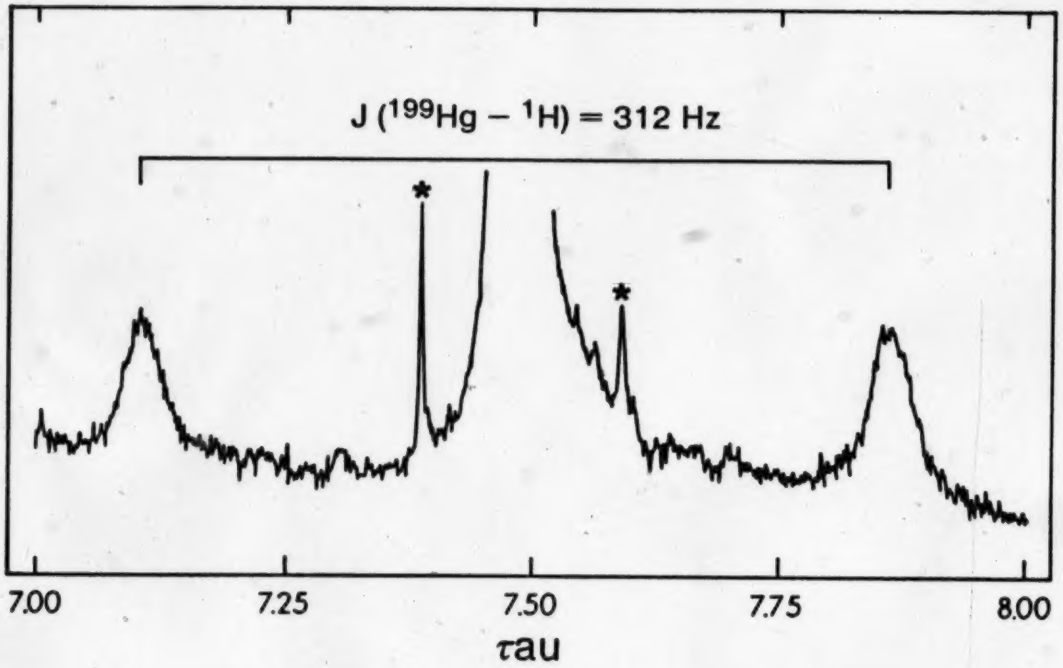


FIGURE 7. 400 MHz ^{1}H NMR spectrum of the methylene resonance of $(NH_3)_5CoNCCH_2Hg(OH_2)^{4+}$ in d_6-dimethylsulfoxide. Asterisks denote spinning side bands.

reaction was found to be first-order in both mercury(II) and complex IV-2. However, the second-order rate constant (k_{obsd}) increases with decreasing $[H^+]$, obeying the rate law

$$k_{obsd} = a + \frac{b}{[H^+]} \quad . \tag{4.24}$$

The experimental rate data are given in Table C-12 of Appendix C. A mechanism consistent with this rate law is

$$\begin{tikzcd}
(NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+} \arrow[rr, shift left, "K_a"] \arrow[dr, "Hg^{2+}", "k_1"'] & & (NH_3)CoNCCH_2Cr(OH_2)_4(OH)^{4+} + H^+ \arrow[rr, phantom] \arrow[ll, shift left] \arrow[dl, "k_2"', "Hg^{2+}"] \\
& (NH_3)_5CoNCCH_2Hg(OH_2)^{4+} + Cr(OH_2)_6{}^{3+} &
\end{tikzcd} \tag{4.25}$$

The predicted rate law gives the second-order rate constant

$$k_{obsd} = \frac{k_1[H^+] + k_2K_a}{K_a + [H^+]} \quad . \tag{4.26}$$

If $K_a << [H^+]$, then the rate law simplifies to

$$k_{obsd} = k_1 + \frac{k_2K_a}{[H^+]} \tag{4.27}$$

which has the same form as that obtained experimentally (equation (4.24)). The values for k_1 and k_2K_a are

$(3.49 \pm 0.19) \times 10^{-2}$ M^{-1} s^{-1} and $(5.8 \pm 1.8) \times 10^{-4}$ s^{-1} (25°C, 1.00 M $LiClO_4$-$HClO_4$), respectively.

Discussion

A summary of the kinetic results obtained in this study is given in Table 15.

The kinetic results for the reaction of chloroacetonitrile and iodoacetonitrile with chromium(II) indicate that the activated complex contains one mole of chromium(II) for each mole of ligand. However, stoichiometry experiments indicate that these ligands are two electron oxidants since two equivalents of chromium(II) are oxidized for each ligand consumed. This suggests that one of the two reactants must proceed through an unstable oxidation state. A possible reaction scheme involves the initial two electron reduction of the ligand.

$$\begin{aligned} NCCH_2X + Cr^{II} &\xrightarrow{H^+} Cr^{IV} + X^- + NCCH_3 \\ Cr^{II} + Cr^{IV} &\longrightarrow (Cr(III))_2 \end{aligned} \qquad (4.28)$$

An intermediate chromium(IV) species[88,90] would be generated which would subsequently react with a second chromium(II) to yield binuclear chromium(III) products, as shown in equation (4.28). However, in the present system, only small amounts of the binuclear product are observed and these can be easily accounted for by the air-oxidation of excess chromium(II). Therefore, it seems reasonable to conclude that an initial two electron redox process does not occur in these systems.

Table 15

Summary of Kinetic Parameters for Formation and Reactions of Some Organochromium(III) Complexes

Reaction[a]	k(25°), $M^{-1}\ s^{-1}$	$\Delta H^{\dagger}$, kcal mol^{-1}	$\Delta S^{\dagger}$, cal $mol^{-1} deg^{-1}$
$NCCH_2I + Cr^{2+}$	9.17	5.44±0.74	-35.8±2.5
$NCCH_2Cl + Cr^{2+}$	1.07×10^{-2}		
$(H_2O)_5CrCH_2CN^{2+} + Cr^{2+}$	$1.73 \times 10^{-2} + \frac{5.62 \times 10^{-4}}{[H^+]}$		
$(NH_3)_5CoNCCH_2I^{3+} + Cr^{2+}$	45.2	3.80±0.55	-38.2±1.9
$(NH_3)_5CoNCCH_2Cl^{3+} + Cr^{2+}$	8.9×10^{-2}		
$(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+} + Cr^{2+}$	2.39×10^{-3}		
$(H_2O)_5CrCH_2CN^{2+} + Hg^{2+}$ [b]	8.7		
$(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+} + Hg^{2+}$ [b]	$3.49 \times 10^{-2} + \frac{5.8 \times 10^{-4}}{[H^+]}$		

---

[a] Ionic strength 0.50 M ($LiClO_4$-$HClO_4$) unless otherwise noted.

[b] Ionic strength 1.00 M ($LiClO_4$-$HClO_4$).

A more likely mechanism involves a multi-step sequence of one equivalent oxidation-reduction reactions. Such a scheme has been frequently suggested for the reduction of other alkyl halides[33,80,91-93] and involves the initial transfer of the halogen from the alkyl group to chromium(II) according to the reaction

$$NCCH_2X + Cr^{2+} \longrightarrow NCCH_2\cdot + (H_2O)_5CrX^{2+} \quad . \qquad (4.29)$$

Such a reaction scheme is verified by the isolation of the halopentaaquochromium(III) products and the observation that no reduction of free acetonitrile occurs in the presence of chromium(II). That halogen transfer is involved in the initial step of the reaction is inferred also by comparing the relative rates of reaction of the chloroacetonitrile and iodoacetonitrile ligands. Iodoacetonitrile is reduced ca. 850 times faster than chloroacetonitrile, consistent with the lower bond energy for C-I bonds compared to C-Cl bonds.[94] This suggests that the reaction is governed principally by carbon to halogen bond breaking. A similar kinetic difference was observed in the reaction of haloacetic acid derivatives with chromium(II).[34] In addition, Sevcik and Jakubcova[34] found that the reactions of chromium(II) with monohalogenated derivatives of acetic acid, HO_2CCH_2X, have $\Delta S^{\ddagger}$ values essentially unaffected by the nature of X, ($\Delta S^{\ddagger} \simeq -39$ cal mol^{-1} deg^{-1}) but $\Delta H^{\ddagger}$ decreases from 10.2 to

5.4 kcal mol^{-1} on going from X ≡ Cl to I. This suggests considerable C-X bond breaking in the activated complex. It is noteworthy that the activation parameters for the reaction of chromium(II) with HO_2CCH_2I[34] are essentially identical to those for the iodoacetonitrile ligand.

The acetonitrile radical generated by halogen-transfer to chromium(II) subsequently reacts with a second chromium(II). However, considerably less than quantitative recovery of the organochromium(III) species is obtained by this reaction.

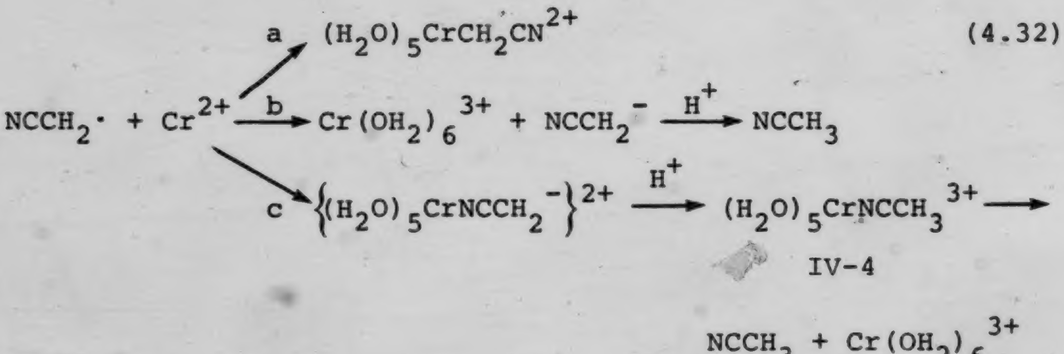
$$NCCH_2\cdot + Cr^{2+} \longrightarrow (H_2O)_5CrCH_2CN^{2+} \qquad (4.30)$$

In the reaction with ICH_2CN, 25% of the ligand is recovered as $(H_2O)_5CrCH_2CN^{2+}$, whereas for $ClCH_2CN$, less than 10% of the organochromium(III) complex is detected. This seems to suggest that there is no common intermediate for these systems since equal yields of the organochromium(III) species would be expected, independent of the nature of the halogen. However, owing to the much slower reactions of the chloroacetonitrile system, chromium(II) catalyzed aquation of $(H_2O)_5CrCH_2CN^{2+}$ becomes a problem. Independent experiments indicated that the decomposition of the organochromium(III) complex

$$(H_2O)_5CrCH_2CN^{2+} + Cr^{2+} \xrightarrow{H_3O^+} (H_2O)_6Cr^{3+} + Cr^{2+} + NCCH_3 \qquad (4.31)$$

is indeed competitive with its formation from $NCCH_2Cl$, but not from iodoacetonitrile. This explains the significantly lower yield obtained for the chloroacetonitrile system.

Similar arguments cannot be used to account for the small yield of $(H_2O)_5CrCH_2CN^{2+}$ obtained from the reduction of iodoacetonitrile since subsequent reactions are not competitive with its formation. As such, the 25% of the organochromium(III) complex indicates that other pathways of reduction are available to the acetonitrile radical. A possible reaction scheme is the following:



$$\begin{aligned}
NCCH_2\cdot + Cr^{2+} &\xrightarrow{a} (H_2O)_5CrCH_2CN^{2+} \\
NCCH_2\cdot + Cr^{2+} &\xrightarrow{b} Cr(OH_2)_6^{3+} + NCCH_2^{-} \xrightarrow{H^+} NCCH_3 \\
NCCH_2\cdot + Cr^{2+} &\xrightarrow{c} \left\{(H_2O)_5CrNCCH_2^{-}\right\}^{2+} \xrightarrow{H^+} \underset{\text{IV-4}}{(H_2O)_5CrNCCH_3^{3+}} \longrightarrow NCCH_3 + Cr(OH_2)_6^{3+}
\end{aligned} \qquad (4.32)$$

Pathway a is the radical coupling reaction of chromium(II) with the acetonitrile radical, and has been described previously. Both pathways b and c lead to the formation of acetonitrile and $Cr(OH_2)_6^{3+}$, both of which were observed in product analysis experiments. Reaction b corresponds to reduction of the acetonitrile radical by a non-bridged-outer-sphere mechanism, yielding the acetonitrile anion which would subsequently react with acid to yield free acetonitrile. Alternatively, reaction c suggests that chromium(II) can coordinate at the nitrile function and subsequently reduce the coordinated radical. The chromium(III) bound acetonitrile anion might then be expected to protonate rapidly, yielding the chromium(III) acetonitrile complex IV-4. Chromium(III) nitrile intermediates have been observed previously, but are subject to either rapid aquation[95] or further reduction in which the nitrile-chromium bond is destroyed.[26] On this basis, decomposition of IV-4 to the observed products would be expected.

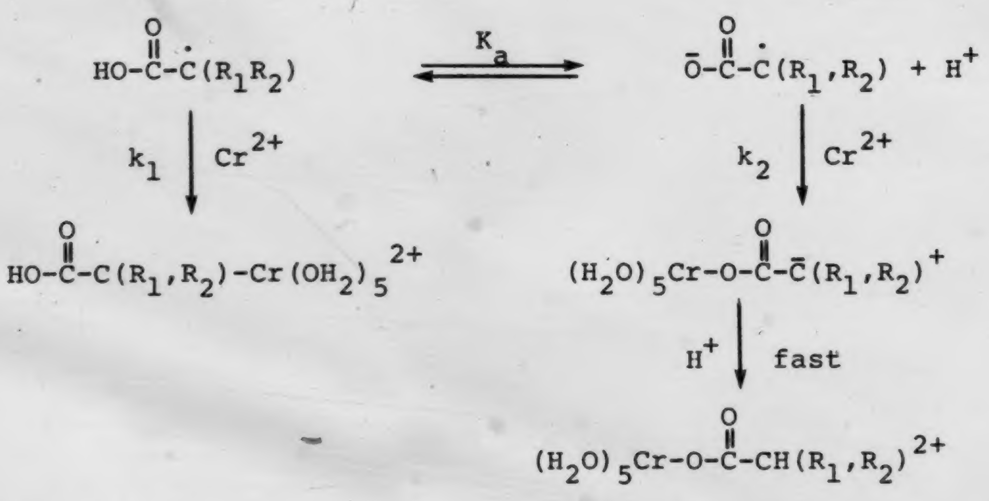
Distinguishing between pathways b and c is not trivial. However, the observation that almost quantitative recovery of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, IV-2, is observed for the reaction of chromium(II) with $(NH_3)_5CoNCCH_2I^{3+}$ suggests that pathway c may be the dominant one. If the $(NH_3)_5Co^{3+}$ moiety is considered as a blocking group on the nitrile function, then the essentially complete recovery of IV-2 in the cobalt(III) system is not surprising if the only alternative reaction pathway for reduction is attack at the nitrile group. On the other hand, for the free acetonitrile radical, the nitrile function is not blocked, and a large percentage of the reduction can occur by prior coordination at the nitrile group. If simple outer-sphere reduction (pathway b) accounted for the low yield of $(H_2O)_5CrCH_2CN^{2+}$ in the reduction of $NCCH_2\cdot$, then a similarly low yield might have been anticipated in the cobalt(III) analogue.

Low yields of organochromium(III) complexes have been observed in other systems. In a series of papers, Sevcik and coworkers[34,96,97] noted that the yields of the organochromium(III) products $(H_2O)_5Cr\text{-}R^{2+}$ obtained from halogenated derivatives of acetic acid decreased in the following manner: $R = HO_2CCH_2\text{-}$, 99%; $HO_2CCHCl\text{-}$, $\leq 40\%$; $HO_2CCCl_2\text{-}$, $\leq 20\%$. It was suggested[97] that these low yields arose from the rearrangement of carbon-centered radicals such as $HOOC\underset{\bullet}{C}Cl_2$ to the more stable oxygen-centered radical $\underset{\bullet}{O}OCCHCl_2$. The latter species could react with chromium(II) according to the reaction

$$Cr^{2+} + \underset{\bullet}{O}OCCHCl_2 \longrightarrow (H_2O)_5CrOOCCHCl_2{}^{2+} \ . \qquad (4.33)$$

This would account for the low yields of organochromium(III) species in such systems. However, ESR results indicate that while the odd electron is increasingly delocalized over the radical in this series, it is still primarily associated with the methylene carbon.[98] As a result, radical rearrangement does not seem to be an acceptable explanation for these observations.

Alternatively, the variation in yield with halogen substitution might be due simply to the variation in acidity of the radicals. The following reaction scheme could account for the observations:


K_a
HO-C(=O)-Ċ(R1R2)
Ō-C(=O)-Ċ(R1,R2) + H+
k1
Cr2+
k2
Cr2+
HO-C(=O)-C(R1,R2)-Cr(OH2)5 2+
(H2O)5Cr-O-C(=O)-C̄(R1,R2)+
H+
fast
(H2O)5Cr-O-C(=O)-CH(R1,R2)2+

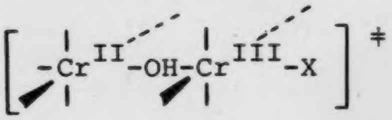
$R_1,R_2 \equiv$ H or Cl (4.34)

Then, the product ratio is given by the expression

$$\frac{[(H_2O)_5CrC(R_1,R_2)CO_2H^{2+}]}{[(H_2O)_5CrO_2CH(R_1,R_2)^{2+}]} = \frac{k_1[H^+]}{k_2K_a} \quad . \qquad (4.35)$$

The value of K_a for the radical would be expected to be similar to that of the parent acid[99] and should increase with increasing halogen substitution. Then, for experiments at constant $[H^+]$, the amount of organochromium(III) product should decrease with increasing halogen subtitution, as observed by Sevcik _et_ _al_.[34,96,97] Of course, variations in k_1 and k_2 also affect the product distribution. The $[H^+]$ dependence of the products could differentiate the two suggestions, but this was not studied by Sevcik _et_ _al_.[34,96,97]

The reaction of $(H_2O)_5CrCH_2CN^{2+}$ with Cr^{2+} was found to exhibit both an acid independent and an inverse acid dependent term in the rate law. Similar kinetic behaviour has been observed in a variety of other Cr^{2+}-CrX^{2+} systems,[86,100-103] some of which are listed in Table 16. The inverse acid term in these systems is believed to arise from an inner-sphere electron transfer process through an activated complex of the type



.

On the other hand, a wide variety of mechanisms have been proposed to account for the acid independent term observed in these systems. It should be noted that the magnitude of the acid independent rate constant (k_1 in Table 16) shows very little variation with the nature of X. This suggests that the hetero-ligand is not directly involved in the acid independent path and an outer-sphere mechanism is the simplest explanation.

Clearly, the results obtained for the reduction of $(H_2O)_5CrCH_2CN^{2+}$ deviate from the pattern just described. Although the form of the rate law is similar to that observed in the other systems, the acid independent term is several orders of magnitude larger than in the other systems, and the inverse acid term is larger than would be expected on the basis of non-bridging ligand effects.

Table 16

Kinetic Parameters for the Chromium(II) Catalyzed Aquation of Various $(H_2O)_5CrX^{2+}$ Complexes[a]

X	$10^5 \times k_1$,[b] $M^{-1}\ s^{-1}$	$10^4 \times k_2$,[c] s^{-1}	Reference
OH_2	<2.0	1.1	100
NH_3	2.4	0.59	101
$^-O_2CCH_3$	1.56	0.25	102
F^-	4.4[d]	0.08	86
N_3^-	52.[d]	0.34	85
$^-CH_2CN$	1730	5.6	This work

[a] Temperature is 25°C unless otherwise noted.

[b] Values reported are for the acid independent path.

[c] Values reported are for the inverse acid dependent path.

[d] Temperature is actually 40°C.

It has been suggested[104] that for cobalt(III) and chromium-(III) complexes, the incoming electron is accepted into the d_{z^2} orbital, and this electron transfer will take place more readily the lower the energy of the d_{z^2} orbital. For $(H_2O)_5CrX^{2+}$ systems, the orbital energy can be lowered either (a) by X^- being a weak field ligand or (b) by movement of the ligands away from the metal atom in the d_{z^2} direction.[105] However, neither explanation readily accounts for the enhanced reactivity when X = $-CH_2CN$. Firstly, the visible spectrum indicates that $-CH_2CN$ is the strongest field ligand in this series and as such would be expected to react the slowest if condition (a) were operative. Furthermore, if condition (b) were in effect and if it is assumed, as others have done,[106] that the ease with which Cr-X bonds can be stretched is related to the ease with which X^- in CrX^{2+} can be replaced by H_2O, then it can be seen that for X = $-CH_2CN$, the Cr-C bond is not easily stretched since no aquation of $(H_2O)_5CrCH_2CN^{2+}$ is observed for several weeks. Indeed, the observed rapid exchange of the trans-H_2O in organochromium(III) systems[107-109] can be taken to imply a very strong Cr-C bond which would not easily be displaced along the d_{z^2} direction. On this basis, $(H_2O)_5CrCH_2CN^{2+}$ would not be expected to be unusually reactive towards reduction by chromium(II). However, with respect to condition (b), it could also be argued that the energy of the acceptor orbital on chromium(III) could be lowered by stretching of the trans $Cr-OH_2$ bond which, as noted above, is readily displaced. In principle, this would provide a means by which facile electron transfer could occur. However, such a formulation is not consistent with the observation that analogous organochromium(III) complexes, such as $(H_2O)_5CrCH_2Cl^{2+}$,[107] are unreactive towards chromium(II).

A scheme consistent with the results involves a bridged-outer-sphere mechanism analogous to that already described for the cyanoacetate complex of pentaamminecobalt(III) (Chapter III). The proposed scheme is the following:

$$\begin{tikzcd}
(H_2O)_5CrCH_2CN^{2+} \arrow[rr, harpoon, shift left, "K_a"] \arrow[d, harpoon, shift left, "K_1\ \ Cr^{2+}"'] & & (HO)(H_2O)_4CrCH_2CN^{+} + H^{+} \arrow[ll, harpoon, shift left] \arrow[d, harpoon, shift left, "K_1'\ \ Cr^{2+}"'] \\
{[(H_2O)_5Cr^{III}CH_2CNCr^{II}]^{4+}} \arrow[u, harpoon, shift left] \arrow[rr, harpoon, shift left, "K_a'"] \arrow[dr, "k_1"] & & {[(HO)(H_2O)_4Cr^{III}CH_2CNCr^{II}]^{3+}} \arrow[u, harpoon, shift left] \arrow[ll, harpoon, shift left] \arrow[dl, "k_2"'] \\
& Cr^{2+} + \bar{C}H_2CNCr(OH_2)_5^{2+} \arrow[d, "H^{+}"'] & \\
& CH_3CNCr(OH_2)_5^{3+} \arrow[d, "H_2O"'] & \\
& CH_3CN + Cr(OH_2)_6^{3+} &
\end{tikzcd} \qquad (4.36)$$

The scheme suggests that a series of pre-equilibria are rapidly established involving deprotonation of a bound OH_2 on the chromium(III) moiety and complexation of chromium(II) on the nitrile. Reduction yields the chromium(III) acetonitrile anion which would be expected to protonate and aquate rapidly in comparison to the initial electron transfer reaction.

The derived rate law for this mechanism is

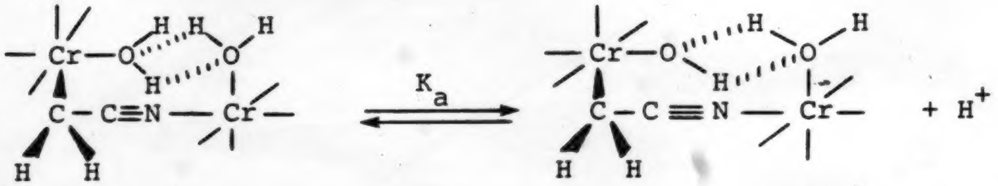
$$k = \frac{(k_1[H^+] + k_2K_a')\ K_1[Cr^{2+}]}{[H^+] + K_a + K_1[Cr^{2+}]([H^+] + K_a')} \qquad (4.37)$$

If $[H^+] >> K_a + K_1[Cr^{2+}]([H^+] + K_a')$, then the rate law simplifies to

$$k = (k_1 + \frac{k_2K_a'}{[H^+]})\ K_1[Cr^{2+}] \qquad (4.38)$$

which is of the same form as found experimentally (equation (4.10)). However, the form of the rate law is such that the inverse acid dependent term may arise from either the K_aK_1' or the $K_a'K_1$ equilibria, or a combination of both.

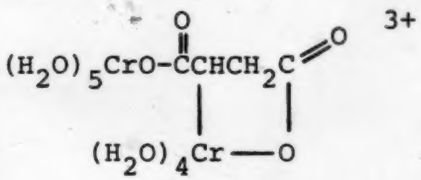
Scheme (4.36) readily accounts for the enhanced reactivity of this system. The bridged intermediate provides close approach of the two metal centres, thereby facilitating direct electron transfer between them. Perhaps more importantly, there is the possibility of hydrogen-bonding between the water molecules coordinated to both metal centres. Molecular models indicate that there is always one cis water molecule on the chromium(III) which is within the hydrogen-bonding distance of a cis water molecule on the chromium(II). This interaction might be expected to facilitate the acid dissociation of bound water within the bridged intermediate.



(4.39)

The enhanced reactivity of the inverse acid dependent path in the rate law could be attributed to such hydrogen-bonding interactions. This should lower the energy barrier to electron transfer by coupling the bond dislocations at both metal centres. This facilitates the matching of the energies of reductant and oxidant,[110] a requirement that must be met before direct electron transfer by a bridged-outer-sphere mechanism can occur. In addition, interactions such as those shown in scheme (4.39) would be expected to increase K_a as compared to the acid dissociation constant that might be anticipated had hydrogen bonding not been possible. This would also contribute to the magnitude of the inverse acid dependent path.

The bridged-outer-sphere mechanism is consistent with the results for other organochromium(III) complexes as well. For example, $(H_2O)_5CrCH_2CO_2H^{2+}$ is reduced with a second-order rate constant of 6.8×10^{-3} M^{-1} s^{-1} (20°C, 0.50 M $HClO_4$) and is believed to yield $(H_2O)_5CrO_2CCH_3^{2+}$ as product.[111] Unfortunately, no attempt was made to establish the acid dependency of this reaction. Nevertheless, the results would seem to suggest that chromium(II) binds at the remote carboxylate group and reduces the carbon-bonded $(H_2O)_5Cr^{3+}$ moiety by a bridged-outer-sphere mechanism. Inner-sphere reduction is unlikely owing to the presence of a saturated methylene group in the ligand. Similar behaviour has been observed for the reaction of chromium(II) with $(H_2O)_5CrCH(Cl)CO_2H^{2+}$,[96] and complex IV-5.[112]



IV-5

However, unlike the earlier example, reduction of complex IV-5 by attack of chromium(II) on the bound carboxylate may proceed by an inner-sphere mechanism.

On the other hand, complexes such as $(H_2O)_5CrR^{2+}$, R ≡ $-CH_2Cl$[107] and $-CCl_3$[113] are apparently unreactive towards chromium(II). These complexes differ from

$(H_2O)_5CrCH_2CN^{2+}$ and the acetic acid derivatives described above in that they lack functional groups suitable for the coordination of a chromium(II). As such, they cannot undergo bridged-outer-sphere reduction and this may account for their lack of reactivity towards chromium(II). The lack of simple outer-sphere reactivity may result from the strong ligand field characteristics of these carbon-bonded species. This makes the acceptor orbitals on the metal of such high energy that electron transfer by a non-bridged-outer-sphere mechanism becomes unfavourable. However, it must be noted that these conclusions are based on a limited number of systems. Additional studies on other organochromium(III) complexes are required to substantiate this proposal.

The results of the study of the reactions of chromium(II) with the chloroacetonitrile and iodoacetonitrile complexes of $(NH_3)_5Co^{3+}$ indicate that these systems show both similarities and differences to the results of the free ligands. Stoichiometry experiments indicate that reduction of $(NH_3)_5CoNCCH_2I^{3+}$ parallels that of the free ligand in that two moles of chromium(II) are consumed per mole of cobalt(III) complex. In addition, the rate law exhibits a first-order dependency on the concentrations of both chromium(II) and the cobalt(III) complex. Since dimeric chromium(III) products are not observed, a mechanism involving chromium(IV) is not operative, and the reaction must proceed as follows:

$$(NH_3)_5CoNCCH_2I^{3+} + Cr^{2+} \longrightarrow (NH_3)_5CoNCCH_2{}^{3+}\cdot + (H_2O)_5CrI^{2+} \quad . \qquad (4.40)$$

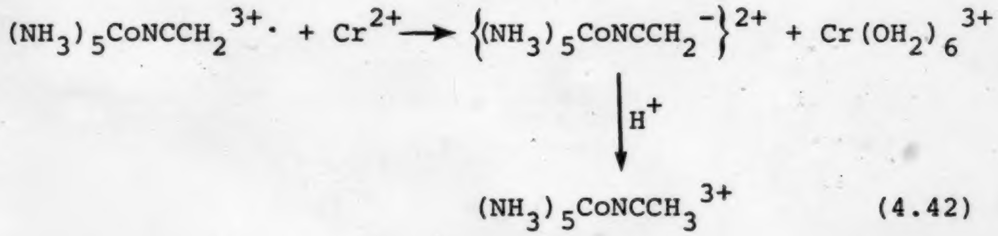
Indeed, $(H_2O)_5CrI^{2+}$ was observed spectrophotometrically and complete recovery of free I^- from aquation of $(H_2O)_5CrI^{2+}$ was obtained. Product analysis results for the chloroacetonitrile complex are less definitive because of the competing outer-sphere reduction of the complex. Nevertheless, the results suggest that halogen transfer to chromium(II) constitutes a major portion of the reaction.

It is interesting to note that the reactivities of these complexes with chromium(II) are appreciably larger than for the respective free ligands. This suggests additional weakening of the C-X bonds upon complexation to $(NH_3)_5Co^{3+}$. This weakening is also exhibited in the values of $\Delta H^{\ddagger}$ for the iodoacetonitrile systems where a decrease of 1.6 kcal mol^{-1} is noted on complexation. On the other hand, the entropy of activation is unaffected by coordination to $(NH_3)_5Co^{3+}$. The five-fold increase in the rate constant on complexation of iodoacetonitrile would predict a halogen abstraction rate constant of ca. $5 \times 10^{-2}\ M^{-1}\ s^{-1}$ for the chloroacetonitrile complex. The difference from the observed value of $8.9 \times 10^{-2}\ M^{-1}\ s^{-1}$ is consistent with a competitive outer-sphere reaction pathway as suggested previously.

The observation that almost quantitative recovery of the organochromium(III) product $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ is found in the reaction of the iodoacetonitrile complex with chromium(II) differs dramatically from that observed in the free ligand reaction. This suggests that the reaction

$$(NH_3)_5CoNCCH_2^{3+}\cdot + Cr^{2+} \longrightarrow (NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+} \qquad (4.41)$$

is highly favoured over a process of simple outer-sphere reduction



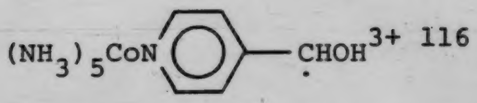
$$(NH_3)_5CoNCCH_2^{3+}\cdot + Cr^{2+} \longrightarrow \{(NH_3)_5CoNCCH_2^{-}\}^{2+} + Cr(OH_2)_6^{3+}$$
$$\{(NH_3)_5CoNCCH_2^{-}\}^{2+} \xrightarrow{H^+} (NH_3)_5CoNCCH_3^{3+} \qquad (4.42)$$

which produces less than 5 percent of the acetonitrile complex. As described earlier, this suggests a special role for the uncoordinated nitrile group in the reduction of the free ligand radical.

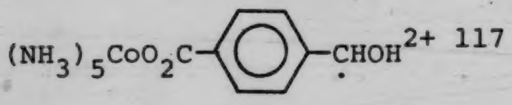
The essentially quantitative recovery of the dimetallic organochromium(III)-cobalt(III) complex was unexpected. It was anticipated that the radical generated by halogen abstraction would undergo intramolecular electron transfer according to the reaction

$$(NH_3)_5CoNCCH_2{}^{3+}\cdot \longrightarrow 5\ NH_3 + Co^{2+} + NCCH_2{}^{+} \xrightarrow{H_2O} NCCH_2OH + H^{+} \quad . \qquad (4.43)$$

That it does not do so is particularly surprising since ESR studies on free $NCCH_2\cdot$ indicate that considerable unpaired spin density resides on the nitrile nitrogen.[114,115] If the coordinated radical is similar, then it seems surprising that it does not reduce the strongly oxidizing cobalt(III) centre. Indeed, preferential reduction of cobalt(III) has been observed for the following radicals

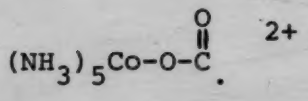


IV-6



IV-7

where the radical oxidizing centres are considerably more separated than in the present system. Intramolecular electron transfer has also been observed in the reaction of $MnO_4{}^-$ with $(NH_3)_5CoO_2CH^{2+}$.[118] In this case, the presumed intermediate is



$$(NH_3)_5Co\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\cdot\ {}^{2+}$$

IV-8

although there is some uncertainty about this assignment.[119] More recently, Srinivasan and Gould[120] have reported other examples of induced intramolecular electron transfer.

On the basis of some results by Cohen and Meyerstein,[81] an upper limit for the rate constant for intramolecular transfer in $(NH_3)_5CoNCCH_2\cdot$ can be calculated. It was found that the rate constants for the formation of chromium(III) alkyls by reaction of chromium(II) with various carbon-centred radicals are in the range $0.35\text{-}3.5 \times 10^8\ M^{-1}\ s^{-1}$.[81] Assuming that the coordinated radical would react in an analogous manner, and after accounting for the different reagent concentrations and the different charge on the reacting radical, the rate constant for intramolecular electron transfer must be smaller than $3.5 \times 10^3\ s^{-1}$ since no cobalt(II) was detected. This value is appreciably smaller than that found for the radicals IV-6,[116] IV-7[117] and IV-8[121] where values greater than 10^6 to $10^7\ s^{-1}$ were estimated. This illustrates how resistant the radical $(NH_3)_5CoNCCH_2\cdot^{3+}$ is to intramolecular electron transfer and suggests the existence of a significant activation barrier for this process.

This barrier to electron transfer may be thermodynamic in nature. Cohen and Meyerstein[122,123] have shown that radicals such as $\dot{C}O_2^-$ and $\cdot CH_2OH$ readily reduce $(NH_3)_6Co^{3+}$ and $(NH_3)_6Ru^{3+}$, whereas radicals such as $\cdot CH_2CO_2H$ and $\cdot CH(CO_2H)_2$ do not react with either oxidant. The former radicals are highly reducing as evidenced by their half-wave potentials.[124] This results in large part from the thermodynamic stability of their respective oxidized products.

$$\cdot CO_2^- \longrightarrow CO_2 + e^- \qquad (4.44)$$

$$\cdot CH_2OH \longrightarrow H_2C{=}O + H^+ + e^-$$

On the other hand, oxidation of the carboxylate radicals yield unstable carbonium ions.

$$\cdot CH_2CO_2H \longrightarrow {}^+CH_2CO_2H + e^- \qquad (4.45)$$

$$\cdot CH(CO_2H)_2 \longrightarrow {}^+CH(CO_2H)_2 + e^-$$

In this respect, $\cdot CH_2CN$ should resemble the carboxylate radicals since the electron-withdrawing capability of the nitrile group should destabilize the carbonium ion formed by the reaction

$$NCCH_2\cdot \longrightarrow NCCH_2^+ + e^- \quad . \qquad (4.46)$$

Indeed, the ionization potential of $NCCH_2\cdot$ has been reported to be 10.87 eV[125] whereas that for $\cdot CH_2OH$ is only 8.2 eV.[126] This difference of 61 kcal mol^{-1} clearly suggests that $NCCH_2\cdot$ should be resistant to oxidation, and as such, provides an explanation for the absence of intramolecular electron transfer to cobalt(III) in $(NH_3)_5CoNCCH_2\cdot^{3+}$.

As noted earlier, $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, IV-2, exhibits remarkable hydrolytic stability. Simple organochromium(III) complexes show a large variation in their decomposition rates.[72,81,82,127-130] For complexes of the type $(H_2O)_5CrCH_2X^{2+}$ (X = Cl , Br, I),[129] typical half-times for aquation range from 12 to 20 days (25°C, 1.0 M $HClO_4$). As such, it is not surprising that the organochromium(III) moiety in complex IV-2 is stable to aquation. However, it is surprising that the nitrile group coordinated to cobalt(III) in complex IV-2 does not hydrolyze to yield the corresponding carboxamide complex. Most coordinated nitriles undergo hydrolysis over a period of several hours or a few days.[47,60] Indeed, complex IV-2 might be expected to be as susceptible to hydrolysis as $(NH_3)_5CoNCCH_2CN^{3+}$ for which the half time for hydrolysis is 2 hours (25°C, pH 1-3, $\mu = 1.0$ M $NaClO_4$).[60] Certainly the chromium(III) should act as a good electron-withdrawing substituent, and the increased charge of complex IV-2 would also be expected to activate the nitrile to hydrolysis. In addition, molecular models of this complex suggest that cis H_2O molecules coordinated to the chromium(III) are oriented with respect to the nitrile group such that intramolecular attack of coordinated H_2O could occur. Similarly, hydrolysis of a coordinated H_2O could lead to intramolecular attack of coordinated OH^- on the nitrile. This lack of reactivity remains surprising, but there is no doubt that the nitrile function remains intact from the characterization of the mercury(II) derivative.

The reaction of chromium(II) with $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, IV-2, results in the reduction of both the cobalt(III) and chromium(III) centres. Since only simple monophasic behaviour was observed, reduction of the first metal centre must be rate limiting. However, the kinetic results do not indicate which metal is reduced first. This can only be inferred from kinetic comparisons.

An outer-sphere reduction mechanism is consistent with the relatively slow rate of reduction ($k = 2.39 \times 10^{-3}\ M^{-1}\ s^{-1}$) and with the absence of functional groups suitable for reductant binding. Certainly, deprotonation of a coordinated H_2O would provide an inner-sphere pathway for the initial reduction of the chromium(III) centre, but the required inverse acid dependence was not detected kinetically. Rather, since cobalt(III) is a much stronger oxidant than chromium(III), it seems likely that the cobalt(III) centre could be reduced first by an outer-sphere mechanism, according to the reaction

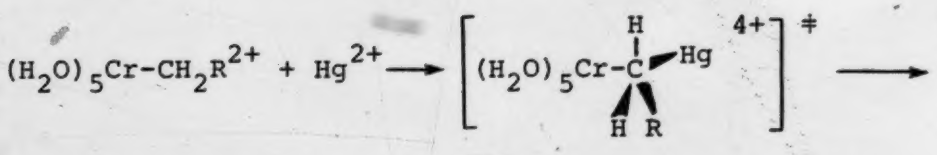
$$\underset{\text{IV-2}}{(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}} + Cr^{2+} \longrightarrow \tag{4.47}$$

$$5NH_3 + Co^{2+} + Cr(OH_2)_6^{3+} + \underset{\text{IV-1}}{(H_2O)_5CrCH_2CN^{2+}}\ .$$

It should be noted that the rate of reduction of complex IV-2 is about ten times slower than other nitrile complexes of $(NH_3)_5Co^{3+}$ which undergo outer-sphere reduction (Chapter III, Table 8). This rate difference might be expected, however, owing to the higher charge of complex IV-2 (5+ as compared to 3+) which would inhibit approach of chromium(II). In any event, scheme (4.47) suggests the initial formation of complex IV-1 whose reactivity towards chromium(II) has already been described. It was shown that the reduction of IV-1 is sufficiently rapid ($k \geq 1.73 \times 10^{-2}\ M^{-1}\ s^{-1}$) to escape detection in the present system. This is consistent with the monophasic absorbance changes observed in the reduction of complex IV-2.

If the order of reduction of the metal centres have been assigned correctly, one must account for the fact that the reduction of $(H_2O)_5CrCH_2CN^{2+}$ is so facile, whereas in $(NH_3)_5CONCCH_2Cr(OH_2)_5{}^{5+}$, the reduction of the chromium(III) centre is inhibited to such an extent that the cobalt(III) centre is preferentially reduced. As described earlier, reduction of $(H_2O)_5CrCH_2CN^{2+}$ probably proceeds by a bridged-outer-sphere mechanism with attack of reductant at the nitrile group. In complex IV-2, the nitrile group is blocked by coordination to cobalt(III) and complexation of chromium(II) is no longer possible. Therefore, normal outer-sphere reduction of the most easily reduced metal, namely cobalt(III), occurs.

The reaction of mercury(II) with organochromium(III) complexes is believed to proceed by an S_E2 mechanism; that is, by a bimolecular electrophilic substitution reaction of mercury(II) at the α-carbon coordinated to chromium(III).[131]



$$(H_2O)_5Cr{-}CH_2R^{2+} + Hg^{2+} \longrightarrow \left[(H_2O)_5Cr{-}\overset{H}{\underset{H\ \ R}{C}}{-}Hg \right]^{4+\ \ddagger} \longrightarrow$$

$$Cr(OH_2)_6{}^{3+} + HgCH_2R^{+} \qquad (4.48)$$

The evidence for such a mechanism is substantial.[79] The observed first order dependence upon $[Hg^{2+}]$ eliminates a unimolecular S_E1 mechanism for which the heterolysis reaction

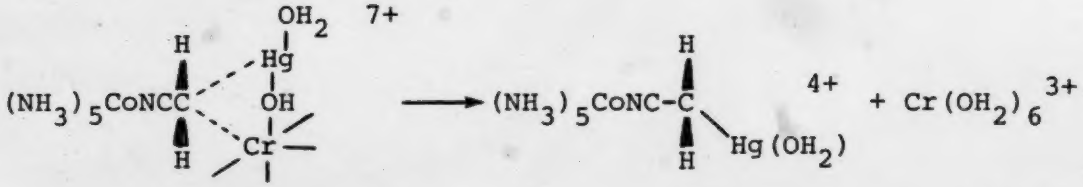
$$(H_2O)_5Cr{-}CH_2R^{2+} \longrightarrow Cr(OH_2)_5{}^{3+} + {}^{-}CH_2R \qquad (4.49)$$

would be rate limiting. The rates of reaction are dramatically decreased as electronegative substituents are added to the α-carbon atom. This is in keeping with an electrophilic process where formal carbanion transfer from chromium to mercury occurs. Clearly, $(H_2O)_5CrCH_2CN^{2+}$ and $(NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+}$ follow this pattern as the following series indicates: $(H_2O)_5CrCH_2CH_3{}^{2+}$ (k = $1.4 \times 10^5\ M^{-1}\ s^{-1}$),[79] $(H_2O)_5CrCH_2OH^{2+}$ ($2.3 \times 10^2\ M^{-1}\ s^{-1}$),[87] $(H_2O)_5CrCH_2CN^{2+}$ ($9.8\ M^{-1}\ s^{-1}$),[87] $(NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+}$ ($\geq 3.5 \times 10^{-2}\ M^{-1}\ s^{-1}$), and $(H_2O)_5CrCF_3{}^{2+}$ ($<10^{-6}\ M^{-1}\ s^{-1}$).[79]

The rate decrease on proceeding from $(H_2O)_5CrCH_2CN^{2+}$ to complex IV-2 is expected on the basis of the electron-withdrawing capability of coordinated $(NH_3)_5Co^{3+}$. In addition, the increased charge of the latter species would be expected to decrease the rate of reaction with mercury(II). However, an inverse acid dependent term in the rate law is observed, suggesting that the reaction of mercury(II) with $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ is more complicated than that observed with other organochromium(III) complexes. A definitive assignment of the mechanism explaining this acid dependency is difficult since there are several functional groups on the complex which could be the source for the acid dependency. However, a consideration of the various possibilities allows some of them to be considered unlikely.

The presence of the electron-withdrawing nitrile group and the $(NH_3)_5Co^{3+}$ and $(H_2O)_5Cr^{3+}$ moieties on the methylene group might enhance the acidity of the methylene group. Reversible deprotonation of the methylene group and mercury(II) attack on the carbanion could produce the inverse acid kinetic term. However, ^1H NMR studies in D_2O indicate that exchange of the methylene protons in $(NH_3)_5CoNCCH_2Hg(OH_2)^{4+}$ is much slower than the reaction of the chromium(III) derivative with mercury(II). Since the acidity of the methylene protons might be expected to be similar in both the chromium and mercury derivatives, the observed slow exchange rate of the methylene protons is inconsistent with the proposed scheme.

The inverse acid dependency would also be consistent with deprotonation of a cis H_2O molecule coordinated to chromium(III) followed by coordination of mercury(II) on the OH^- group. The intermediate (IV-10) could react according to the scheme



IV-10 (4.50)

The orientation of coordinated mercury(II) in IV-10 is such that simultaneous Hg-C bond formation and Cr-C bond-breaking within the intermediate could occur. Such a scheme seems unlikely, however, because of the low affinity of mercury(II) for oxygen donors.[132]

Another explanation for the observed acid dependency also involves deprotonation of a coordinated H_2O molecule on chromium(III). The mercury(II) may react by the normal S_E2 mechanism with the aquo or hydroxy complex.

$$\begin{tikzcd} (\mathrm{NH_3})_5\mathrm{CoNCCH_2Cr(OH_2)_5}^{5+} \arrow[rr, shift left, "K_a"] \arrow[dr, "k_1"', "\mathrm{Hg}^{2+}"] & & (\mathrm{NH_3})_5\mathrm{CoNCCH_2Cr(OH_2)_4(OH)}^{4+} + \mathrm{H}^+ \arrow[ll, shift left] \arrow[dl, "k_2"', "\mathrm{Hg}^{2+}"] \\ & (\mathrm{NH_3})_5\mathrm{CoNCCH_2Hg(OH_2)}^{4+} + \mathrm{Cr(OH_2)_6}^{3+} & \end{tikzcd}$$

(4.51)

Deprotonation of a water molecule could serve three purposes. Firstly, the reduced charge of the deprotonated complex would facilitate approach of the dipositive mercury(II) ion. Secondly, if the deprotonated OH^- group is trans to the organic ligand, the trans-labilizing effect of OH^- would weaken the Cr-C bond and increase its reactivity toward mercury(II). Finally, $Cr(OH_2)_4(OH)^{2+}$ would favour electrophilic attack at coordinated carbon because it would be less electron-withdrawing than $Cr(OH_2)_5{}^{3+}$. Such a scheme is supported by the analogous reaction of $(H_2O)_5CrCl^{2+}$ with mercury(II),[133] where an inverse acid dependency is also observed. Alternatively, the mercury(II) catalyzed aquation of $(NH_3)_5CrCl^{2+}$ [134] and $(NH_3)_5CoCl^{2+}$ [135,136] do not exhibit inverse acid dependencies. This strongly suggests that the acid dependency observed for the $(H_2O)_5CrCl^{2+}$-Hg^{2+} reaction, and by implication for the $(NH_3)_5CoNCCH_2Cr(OH_2)_5{}^{5+}$-$Hg^{2+}$ reaction, arises from deprotonation of a H_2O molecule coordinated to the chromium(III). It also suggests that the acid dependency does not arise from the equilibrium

$$Hg^{2+} \overset{H_2O}{\rightleftharpoons} HgOH^+ + H_3O^+ \qquad (4.52)$$

since it is difficult to explain how $HgOH^+$ could discriminate between $(NH_3)_5CrCl^{2+}$ and $(NH_3)_5CoCl^{2+}$, where no acid dependency is observed, and the complexes $(H_2O)_5CrCl^{2+}$ and

$(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, where an acid dependency is found.

The absence of an inverse acid dependence in the mercury(II) displacement reaction of $(H_2O)_5CrCH_2CN^{2+}$ as well as other simple organochromium(III) complexes can be explained on the basis that the H_2O molecules coordinated to chromium(III) in these complexes are appreciably less acidic than those in $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$. Certainly, the lower charge (2+ as compared to 5+) would tend to decrease the extent of deprotonation. The absence of an inverse acid term for the $(H_2O)_5CrCH_2R^{2+}$ complexes can be accounted for if the acid dissociation constant (K_a) decreases by only a factor of ten, and if the ratio of k_1 to k_2 is the same as for $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$. For the general rate law

$$k_{obsd} = k_1 + \frac{k_2K_a}{[H^+]} \qquad (4.53)$$

and from the values $k_1 = 3.49 \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k_2K_a = 5.8 \times 10^{-4}\ s^{-1}$ for complex IV-2, it can be seen that a ten-fold decrease in K_a would make the inverse acid path insignificant in comparison to the independent acid path over the usual acid range studied.

CHAPTER V

Chromium(II) Reduction of the Fumaronitrile Complex of Pentaamminecobalt(III)

Introduction

Oxidation-reduction reactions in which the electron transfer occurs through a bridging ligand that is "reducible" are believed to proceed through a chemical mechanism in which ligand reduction is assumed to be rate-determining.[21,137,138] A number of systems thought to proceed in this manner have been previously reported.[24,26,32,48,139-143] In addition, many potential bridging ligands are themselves reactive toward external reductants when uncomplexed.[24,36,37,143-148] Since fumaronitrile is known to be "reducible",[149] detailed kinetic studies were undertaken to ascertain the reactivity of free fumaronitrile as well as its $(NH_3)_5Co^{3+}$ complex toward chromium(II).

Experimental

The synthesis of the fumaronitrile complex of $(NH_3)_5Co^{3+}$ has been described in Chapter II. Samples of fumaronitrile ligand for kinetic and product analysis studies were twice sublimed under reduced pressure before use.

Product Analyses

Ion-exchange of reaction mixtures on Dowex 50W-X2 and Sephadex SP-C25 cation-exchange resins was done as described in Chapter II.

The nature of the organic reduction products for the reaction of chromium(II) with free fumaronitrile was determined by ^{13}C NMR. Fumaronitrile was allowed to react with acidic solutions of chromium(II) for several hours until the reaction was judged to be complete. Any excess chromium(II) was air-oxidized and the resulting solutions were treated with 6 M NaOH to precipitate chromium(III) as chromium(III) hydroxide. The mixture was centrifuged and the supernatant was collected and reacidified with perchloric acid. Then t-butanol was added as an internal standard and the ^{13}C NMR spectra recorded in 10% D_2O. The sole organic product detected was succinonitrile, as determined by comparison to the spectrum of an authentic sample.

As a further check on the identity of the organic product, reaction mixtures of fumaronitrile and chromium(II) were extracted ten times with CH_2Cl_2. The organic phase was collected, dried over $MgSO_4$, and evaporated to dryness under vacuum. A white product was obtained in 85% yield, based on fumaronitrile, and was characterized by ^1H NMR and infrared spectroscopies. The spectral results were in excellent agreement with samples of succinonitrile.

Quenching Studies

Reaction mixtures of fumaronitrile and chromium(II) were allowed to react for various lengths of time, air-oxidized and charged onto ion-exchange columns. The unreacted fumaronitrile was collected in the initial eluant and the amount of unreacted ligand was determined spectrophotometrically ($\varepsilon_{218} = 1.84 \times 10^4\ M^{-1}\ cm^{-1}$). If the rate law has the form

$$\frac{-d[\mathrm{NCCH{=}CHCN}]}{dt} = k[\mathrm{NCCH{=}CHCN}][\mathrm{Cr}^{2+}]^2 \qquad (5.1)$$

and assuming the stoichiometry is

$$2\mathrm{Cr}^{2+} + \mathrm{NCCH{=}CHCN} \longrightarrow \mathrm{Products} \qquad (5.2)$$

then the general equation (5.3) may be derived.[150]

$$\frac{1}{([Cr^{2+}]_o-2[L]_o)}\left\{\frac{1}{[Cr^{2+}]_o} - \frac{1}{[Cr^{2+}]_f}\right\} + \left[\frac{1}{([Cr^{2+}]_o - 2[L]_o)^2}\right] \ln\left\{\frac{[L]_o[Cr^{2+}]_f}{[L]_f[Cr^{2+}]_o}\right\} = kt \qquad (5.3)$$

where $[Cr^{2+}]_o$ and $[Cr^{2+}]_f$ are the initial and final concentrations of chromium(II), $[L]_o$ and $[L]_f$ are the initial and final concentrations of fumaronitrile, t is the time in seconds and k is the third-order rate constant ($M^{-2}\ s^{-1}$). From the known initial concentrations $[Cr^{2+}]_o$ and $[L]_o$, and the final concentration $[L]_f$ and the time of reaction , t, k can be determined.

Results

$(NH_3)_5CoNCCH{=}CHCN^{3+} + Cr^{2+}$

The chromium(II) reduction of the fumaronitrile complex of $(NH_3)_5Co^{3+}$ was so rapid that it was necessary to establish the rate law primarily under second-order conditions in which only small excesses of chromium(II) were present. The absorbance-time curves obtained at 260 nm were treated as described in Chapter II. The results obtained under both second-order and pseudo-first-order conditions revealed that the reaction obeyed the rate law

$$\frac{-d[(NH_3)_5CoNCCH{=}CHCN^{3+}]}{dt} = k[(NH_3)_5CoNCCH{=}CHCN^{3+}][Cr^{2+}] \ . \tag{5.4}$$

The rate data are summarized in Table C-13 of Appendix C and the second-order rate constant (k) was determined to be $(1.9 \pm 0.2) \times 10^5\ M^{-1}\ s^{-1}$ (25°C, 0.50 M $LiClO_4$-$HClO_4$).

A product analysis study was undertaken to determine the products of the reduction. A solution of $(NH_3)_5CoNCCHCHCN^{3+}$ (1.95×10^{-3} M) in 0.10 M $HClO_4$ was allowed to react with chromium(II) (2.15×10^{-3} M). The solution was immediately air-oxidized and subjected to ion-exchange chromatography on Dowex 50W-X2 resin at 5°C.

The initial eluant was collected and analyzed for free fumaronitrile which has a characteristic absorption band at 218 nm ($\varepsilon = 1.84 \times 10^4\ M^{-1}\ cm^{-1}$). Two bands were observed on the column with elution properties and electronic spectra characteristic of Co^{2+} and $Cr(OH_2)_6{}^{3+}$, respectively. The relative yields of fumaronitrile, Co^{2+} and $Cr(OH_2)_6{}^{3+}$ were found to be 98%, 101% and 102%, respectively.

These results suggest that the reaction proceeds according to scheme (5.5).

$$(NH_3)_5CoNCCHCHCN^{3+} + Cr^{2+} \longrightarrow$$
$$5NH_3 + Co^{2+} + Cr(OH_2)_6{}^{3+} + NCCHCHCN \qquad (5.5)$$

However, repetitive scans of reaction mixtures containing a slight deficiency of chromium(II) revealed the initial formation of a species which exhibited a wavelength maximum at 395 nm with an approximate molar extinction coefficient of 25 $M^{-1}\ cm^{-1}$. Over a period of only a few minutes, the intensity of this band decreased and the maximum shifted to 408 nm, suggesting decomposition of the intermediate to $Cr(OH_2)_6{}^{3+}$. The spectrum of the intermediate species is suggestive of nitrogen coordination when compared to the spectrum of $(H_2O)_5CrNH_3{}^{3+}$ [101] and is consistent with the species

$$(H_2O)_5CrN{\equiv}CCH{=}CHC{\equiv}N^{3+}.$$

V-1

Aquation of $(H_2O)_5CrNCCH{=}CHCN^{3+}$

The decomposition of complex V-1 was investigated further at 395 nm and the data is compiled in Table C-14 of Appendix C. The reaction was found to be independent of the chromium(II) concentration (0.87×10^{-3} to 3.58×10^{-3} M) and obeyed the rate law

$$k_{obsd} = \left(a + \frac{b}{[H^+]} \right) [V\text{-}1] \tag{5.6}$$

A plot of k_{obsd} vs $[H^+]^{-1}$ is shown in Figure 8. The kinetic behaviour and the product analysis results are consistent with the reaction scheme

$$\begin{tikzcd}
(H_2O)_5CrN{\equiv}CCH{=}CHC{\equiv}N^{3+} \arrow[rr, shift left, "K_a"] \arrow[dr, "k_1"'] & & (HO)(H_2O)_4CrN{\equiv}CCH{=}CHC{\equiv}N^{2+} + H^+ \arrow[ll, shift left] \arrow[dl, "k_2"] \\
& N{\equiv}CCH{=}CHC{\equiv}N + Cr(OH_2)_6^{3+} &
\end{tikzcd} \tag{5.7}$$

From a consideration of the normal acidity of water coordinated in aquochromium(III) complexes and the range of $[H^+]$ studied (0.025 to 0.442 M), it is reasonable to assume that $[H^+] \gg K_a$, so that scheme (5.7) predicts that

$$k_{obsd} = k_1 + \frac{k_2 K_a}{[H^+]} \quad . \tag{5.8}$$

This is the form found experimentally and a non-linear least-squares analysis of the data yields

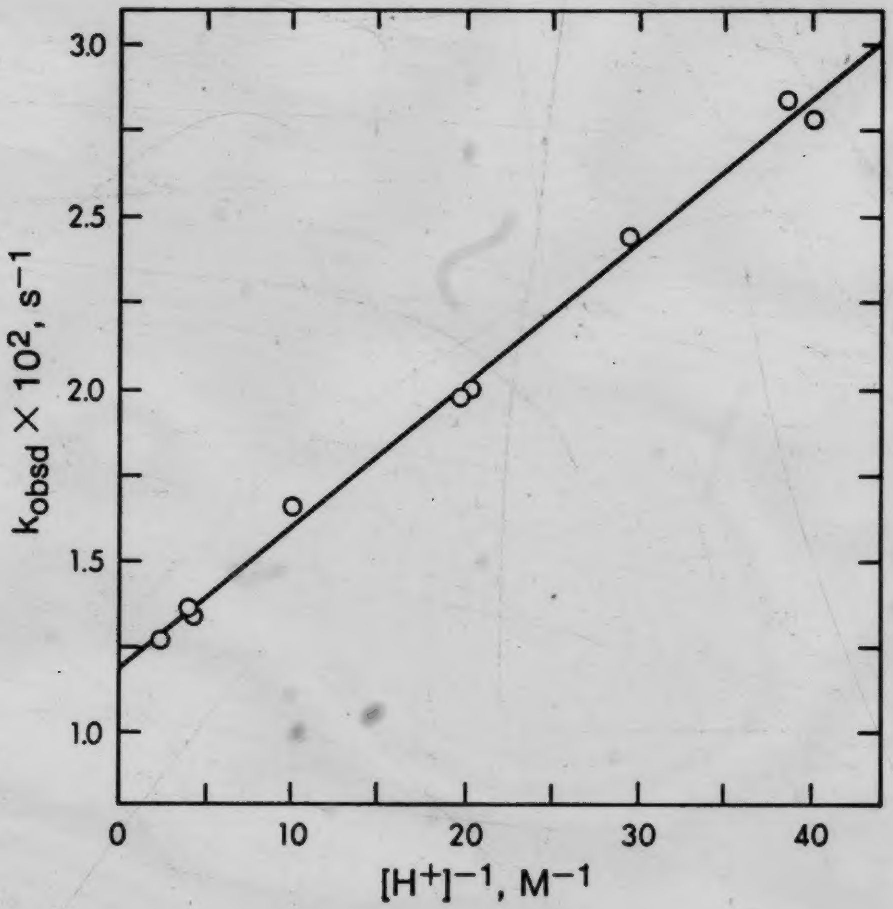


FIGURE 8. Variation of k_{obsd} with $[H^+]^{-1}$ for the aquation of $(H_2O)_5CrNCCH{=}CHCN^{3+}$ at 25°C in 0.50 M $LiClO_4$-$HClO_4$.

$k_1 = (1.19 \pm 0.05) \times 10^{-2}\ s^{-1}$ and $k_2K_a = (4.14 \pm 0.34) \times 10^{-4}\ M\ s^{-1}$, (25°C, 0.50 M $LiClO_4$-$HClO_4$).

When large excesses of chromium(II) are present during the reduction of $(NH_3)_5CoNCCHCHCN^{3+}$, quite different behaviour is observed. Instead of a decrease in absorbance throughout the visible spectrum, a large increase in absorbance is observed with maxima in the 410 and 520 nm regions. The intensities of these maxima then decrease slowly. In addition, ion-exchange experiments on reaction mixtures revealed several chromium complexes of different charge and a decrease in the amount of fumaronitrile recovered.

In order to better understand the behaviour with excess chromium(II), the reaction of free fumaronitrile and chromium(II) was studied. It should be noted at the outset that free fumaronitrile reacts several orders of magnitude more slowly with chromium(II) than does the reduction product of the cobalt(III) complex.

$NCCH{=}CHCN + Cr^{2+}$

The reaction between chromium(II) and uncomplexed fumaronitrile exhibits biphasic kinetic behaviour. A representative absorbance-time trace is shown in Figure 9. Stoichiometry experiments were undertaken to ascertain at which stage chromium(II) was consumed. The stoichiometry results in Table 17 indicate that two moles of chromium(II)

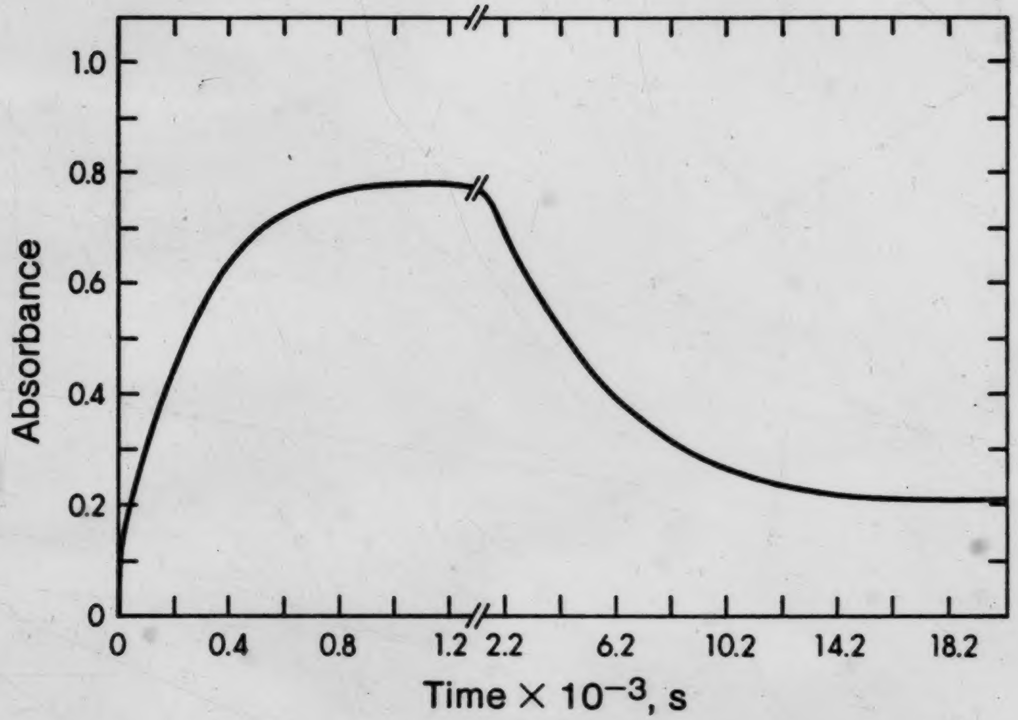


FIGURE 9. A plot of absorbance change *versus* time for the reaction of NCCH=CHCN (1.85×10^{-3} M) with chromium(II) (3.23×10^{-2} M) at 520 nm; $[H^+]$ = 0.075 M; 25°C; Ionic strength 0.50 M ($LiClO_4$); 5 cm cell.

Table 17

Stoichiometry Results for Reaction of Chromium(II) with NCCH=CHCN.

[NCCH=CHCN], M	$[Cr^{2+}]$, M	$[H^+]$, M	Rx. Time, min	$[Cr^{2+}]_{left}$,[a] M	$[Cr^{2+}]_{consumed}$, M	$\frac{[Cr^{2+}]_{consumed}}{[NCCH=CHCN]}$
0.0271	0.103	0.483	19.5[b]	0.0486	0.0544	2.01
0.0271	0.103	0.097	19.5[b]	0.0482	0.0548	2.02
0.0219	0.0956	0.103	210[c]	0.0509	0.0447	2.04

[a] Determined by adding excess Fe^{3+} and titrating the excess Fe^{3+} iodometrically with sodium thiosulfate.

[b] After first reaction is complete.

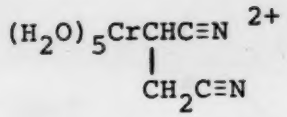
[c] After second reaction is complete.

are consumed for each mole of fumaronitrile during the reaction resulting in the initial rise in absorbance. Subsequent reactions associated with the absorbance decrease do not consume any additional chromium(II). Similar results were obtained when fumaronitrile was in excess, thereby suggesting that radical coupling of the ligand is not a significant problem, even when there is a deficiency of reductant.

Several ^{13}C NMR experiments were undertaken to ascertain the nature of the organic reduction products. Reaction mixtures of fumaronitrile and chromium(II) were treated as described in the Experimental Section. The sole organic product detected by ^{13}C NMR was succinonitrile, as determined by comparison to the spectrum of an authentic sample. In other experiments, also described in the Experimental Section, the solid organic product (85%) was isolated and characterized by ^{1}H NMR and infrared spectroscopies. The spectral results were in excellent agreement with samples of succinonitrile.

Preliminary product studies were undertaken to ascertain the nature of the highly-coloured complexes formed during the initial phase of the reduction. Elution of reaction mixtures charged onto columns of Dowex 50W-X2 yielded first a red band (Band 1) which moved down the column with 0.5 M $HClO_4$, followed by a blue band (Band 2) which eluted with 1.0 M $HClO_4$. Several other complexes remained on the column and could not be eluted even with solutions of 1 M $HClO_4$ in 2 M $NaClO_4$. As a result, product analysis experiments were repeated using Sephadex SP-C25 cation-exchange resin. The following elution pattern was observed: a red band (Band 1) was eluted with 0.2 M $HClO_4$; a blue band (Band 2) was eluted with 0.2 M $HClO_4$ in 0.2 M $NaClO_4$; a second red band (Band 3) was eluted with 0.2 M $HClO_4$ in 0.5 M $NaClO_4$; a pinkish-red band (Band 4) and a small purple band (Band 5) would not elute from the column even with 1.0 M $HClO_4$ in 3 M $NaClO_4$. However, on standing for 2 days at room temperature, Band 4 decomposes to products which are easily eluted with 1 M $HClO_4$. Similar decomposition of Band 5 does not occur. It can only be removed from the resin by conversion to chromate using alkaline peroxide.

The isolated complexes were studied in greater detail to obtain additional information about their structure. The easily eluted red species (Band 1) was characterized and found to have maxima at 519, 411, and 268 nm with extinction coefficients of 81.1, 117 and 4090 M^{-1} cm^{-1}, respectively, based on its chromium(III) content. The wavelength maxima and elution properties of this complex are similar to those for $(H_2O)_5CrCH_2CN^{2+}$, which has already been described in Chapter IV. On this basis, the complex is formulated as



$$(H_2O)_5Cr\underset{\substack{|\\ CH_2C\equiv N}}{CH}C\equiv N^{\;2+}$$

V-2

Scan runs of a representative sample of complex V-2 in 0.50 M $HClO_4$ revealed that no decomposition occurs over a period of several weeks at room temperature in the presence of O_2. This organochromium(III) complex reacts with mercury(II) very slowly. A 3.3×10^{-2} M solution of complex V-2 in 0.50 M $HClO_4$ is observed to react with 0.10 M Hg^{2+} with a rate constant of $3.2 \times 10^{-5}\ s^{-1}$. However, complex V-2 is readily reduced by chromium(II), as the scan run of Figure 10 illustrates, and the kinetics of this reaction were studied. The data are given in Table C-15 of Appendix C and conform to the rate law

$$\frac{-d[V\text{-}2]}{dt} = k[V\text{-}2][Cr^{2+}] \qquad (5.9)$$

with $k = (1.19 \pm 0.03) \times 10^{-2}\ M^{-1}\ s^{-1}$ (25°C, 0.50 M $LiClO_4$-$HClO_4$). The sole chromium(III) product of the reaction was $Cr(OH_2)_6^{3+}$ as indicated by its electronic spectrum after isolation by ion-exchange on Dowex 50W-X2.

The blue band (Band 2) was found to be $Cr(OH_2)_6^{3+}$ on the basis of its ion-exchange properties and electronic spectrum.

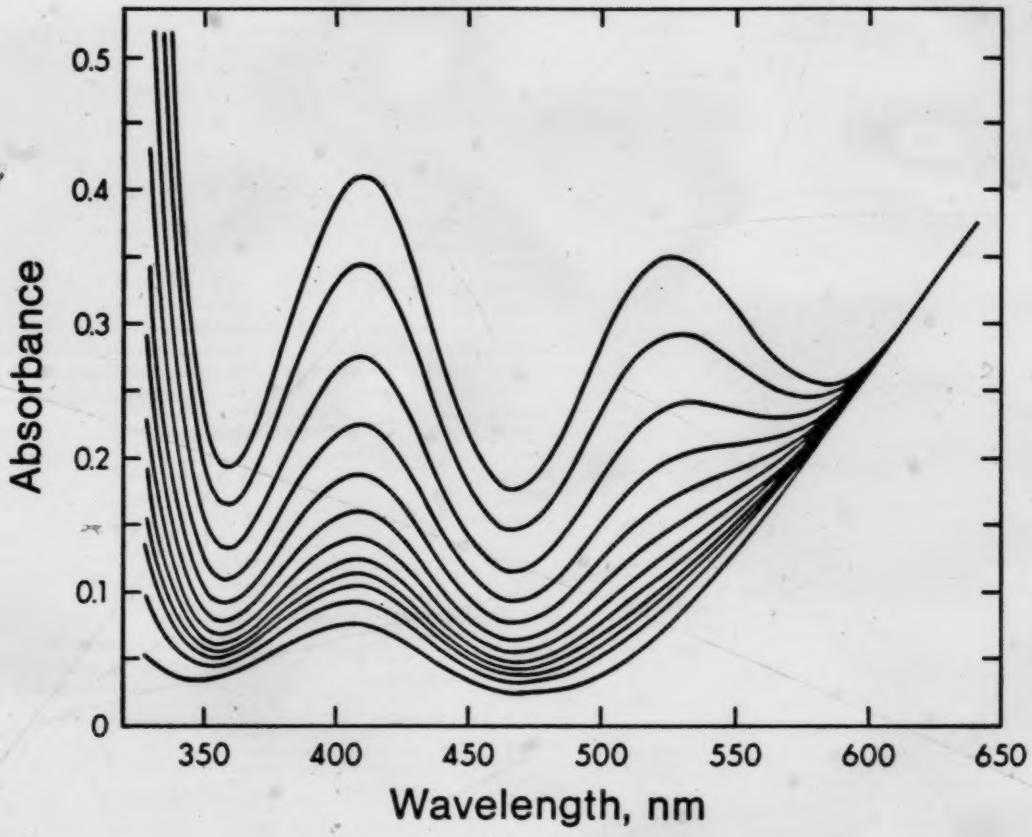
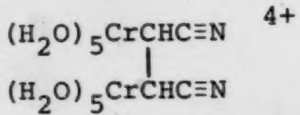


FIGURE 10. Change in visible spectrum during reduction of $(H_2O)_5CrCH(CN)CH_2CN^{2+}$ (2.10×10^{-3} M) with chromium(II) (4.97×10^{-2} M); $[H^+] = 0.20$ M; 25°C; Ionic strength 0.50 M ($LiClO_4$); 2 cm cell. The absorbance is decreasing with time. The spectral scans were started at 1, 9, 17, 25, 33, 41, 49, 57, 65, 73, 89 and 217 minutes after mixing.

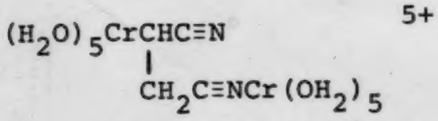
The ion-exchange properties of the red complex (Band 3) are typical of a 4+ or 5+ charged species, suggesting that it is a dichromium(III) complex. The electronic spectrum of this complex revealed maxima at 515, 408 and 267 nm. Assuming two chromium's are coordinated to the organic moiety, molar extinction coefficients of the complex are calculated to be 116, 137 and 4080 M^{-1} cm^{-1}, respectively. It is worth noting that the intensities of the various maxima are either unchanged or only slightly higher than those observed for complex V-2. If the complex formed was



$$\begin{array}{l}(H_2O)_5CrCHC\equiv N\\ \qquad\qquad |\\ (H_2O)_5CrCHC\equiv N\end{array}^{4+} ,$$

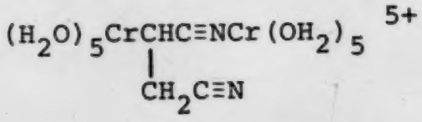
V-3

then it might be anticipated that the extinction coefficient of this complex would be approximately twice that observed for complex V-2, as has been observed in other systems.[35] Since this is not seen in the present system, the complex may be assigned as one of the following linkage isomers.



$$\begin{array}{l}(H_2O)_5CrCHC\equiv N\\ \qquad\qquad |\\ \qquad\qquad CH_2C\equiv NCr(OH_2)_5\end{array}^{5+}$$

V-4

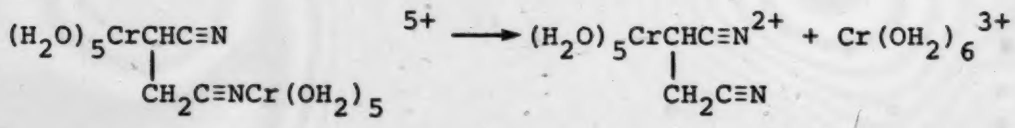


$$\begin{array}{l}(H_2O)_5CrCHC\equiv NCr(OH_2)_5\\ \qquad\qquad |\\ \qquad\qquad CH_2C\equiv N\end{array}^{5+}$$

V-5

Structure V-4 would be preferred on steric grounds and would be expected to be the principal isomer formed.

Repetitive scan runs of solutions of complex V-4 indicated that it underwent facile decomposition. Shown in Figure 11 are the spectra of complex V-4 and that of the hydrolyzed mixture. Isosbestic points were observed at 558, 433 and 408 nm. It is interesting to note that although the intensity of the 515 nm band decreases as a result of the hydrolysis reaction, the spectrum of the product mixture, with maxima at 520 and 411 nm, is still indicative of an organochromium(III) species. Kinetic studies, monitored at 510 nm, revealed that the reaction rate was unaffected by the presence of O_2 and was independent of the acid concentration (0.025 to 0.330 M). The kinetic data, given in Table C-16 of Appendix C, are consistent with a first-order rate law with a rate constant of $(3.60 \pm 0.09) \times 10^{-4}\ s^{-1}$ (25°C, 0.50 M $LiClO_4$-$HClO_4$). Product analysis experiments on this reaction revealed that 1.00 mole of complex V-4 produces 0.99 ± 0.01 mole of a red complex, whose elution properties and electronic spectrum are identical with complex V-2, and 1.01 ± 0.01 mole of $Cr(OH_2)_6^{3+}$. On this basis, the decomposition reaction can be formulated as



$$(\mathrm{H_2O})_5\mathrm{Cr}\underset{\displaystyle|\atop\displaystyle\mathrm{CH_2C{\equiv}NCr(OH_2)_5}}{\mathrm{CH}}\mathrm{C{\equiv}N}^{5+} \longrightarrow (\mathrm{H_2O})_5\mathrm{Cr}\underset{\displaystyle|\atop\displaystyle\mathrm{CH_2C{\equiv}N}}{\mathrm{CH}}\mathrm{C{\equiv}N}^{2+} + \mathrm{Cr(OH_2)_6}^{3+}$$

V-4 V-2 (5.10)

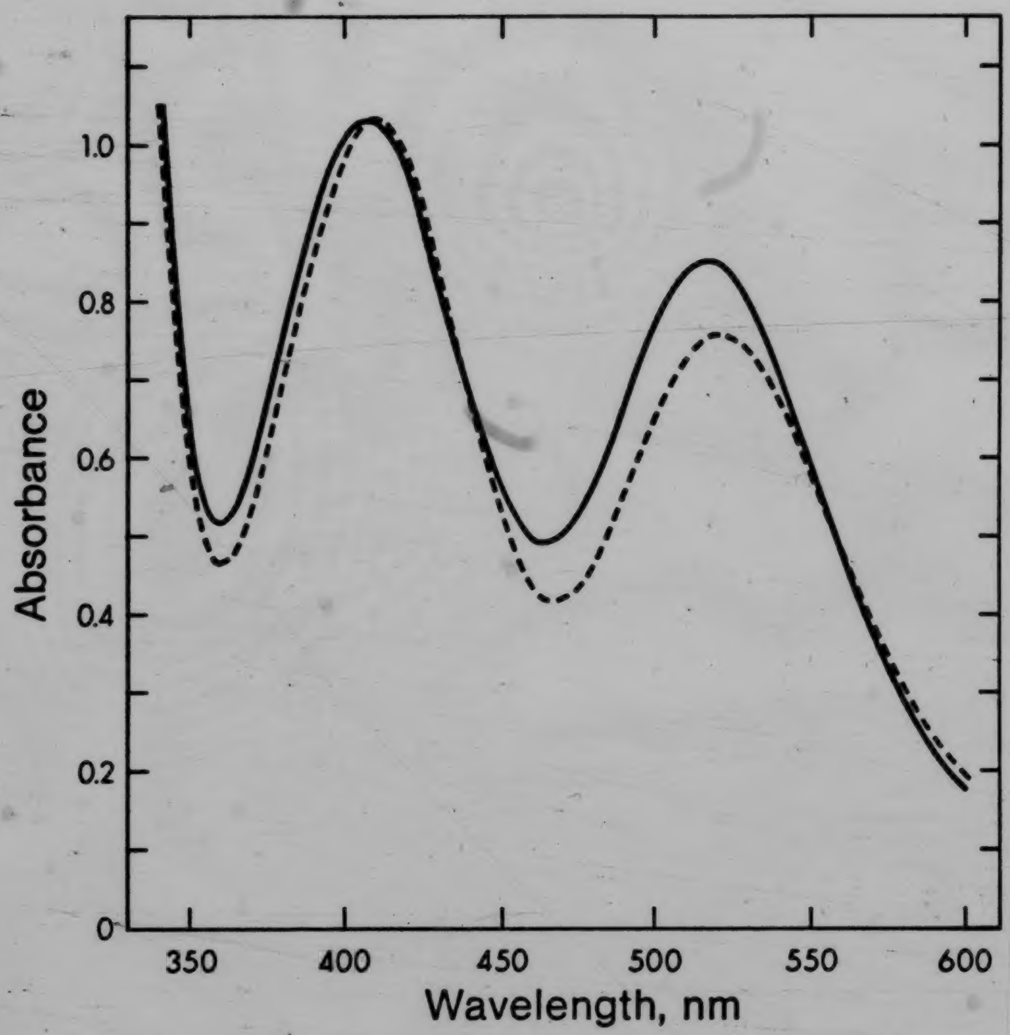
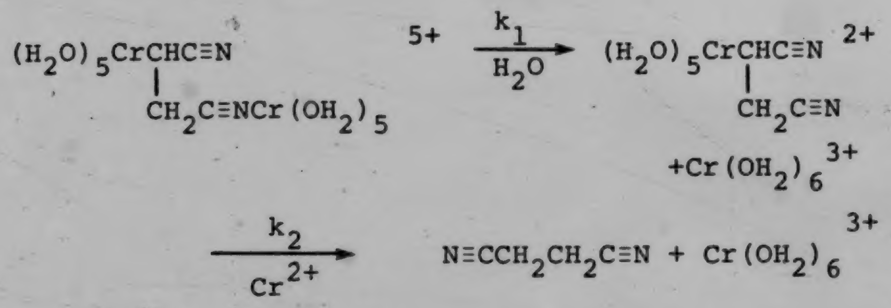


FIGURE 11. Visible spectra of $(H_2O)_5CrCH(CN)CH_2CNCr(OH_2)_5{}^{5+}$ (1.49×10^{-3} M) before (———) and after (-----) aquation; $[H^+]$ = 0.50 M; 25°C; 5 cm cell. Isosbestic points are observed at 558, 433 and 408 nm.

The reactivity of complex V-4 to chromium(II) was also investigated. The reaction was monitored at 408 nm which is an isosbestic point for the conversion of V-4 to V-2. Logarithmic plots of the absorbance change versus time were non-linear as would be expected for a reaction sequence of the type



$$(H_2O)_5CrCH(C\equiv N)CH_2C\equiv NCr(OH_2)_5^{5+} \xrightarrow[H_2O]{k_1} (H_2O)_5CrCH(C\equiv N)CH_2C\equiv N^{2+} + Cr(OH_2)_6^{3+} \xrightarrow[Cr^{2+}]{k_2} N\equiv CCH_2CH_2C\equiv N + Cr(OH_2)_6^{3+} \qquad (5.11)$$

A representative plot is shown in Figure 12. The absorbance-time data was fitted by non-linear least-squares to a two step consecutive reaction scheme where k_2 was held constant at the value $1.19 \times 10^{-2}\ M^{-1}\ s^{-1}$ obtained from the earlier study of the reduction of complex V-2. The values of k_1 generated are given in Table C-17 of Appendix C; k_1 is independent of chromium(II) and has a value of $4.6 \times 10^{-4}\ s^{-1}$. Also shown in Table C-17 for comparison purposes are values of k_1 obtained when k_2 is fixed to the slightly higher value of $1.25 \times 10^{-2}\ M^{-1}\ s^{-1}$. In this case, k_1 seems to exhibit a small dependence on the chromium(II) concentration which may be given by

$$k_1\ (s^{-1}) = 3.6 \times 10^{-4} + 1.8 \times 10^{-3}\ [Cr^{2+}] \qquad (5.12)$$

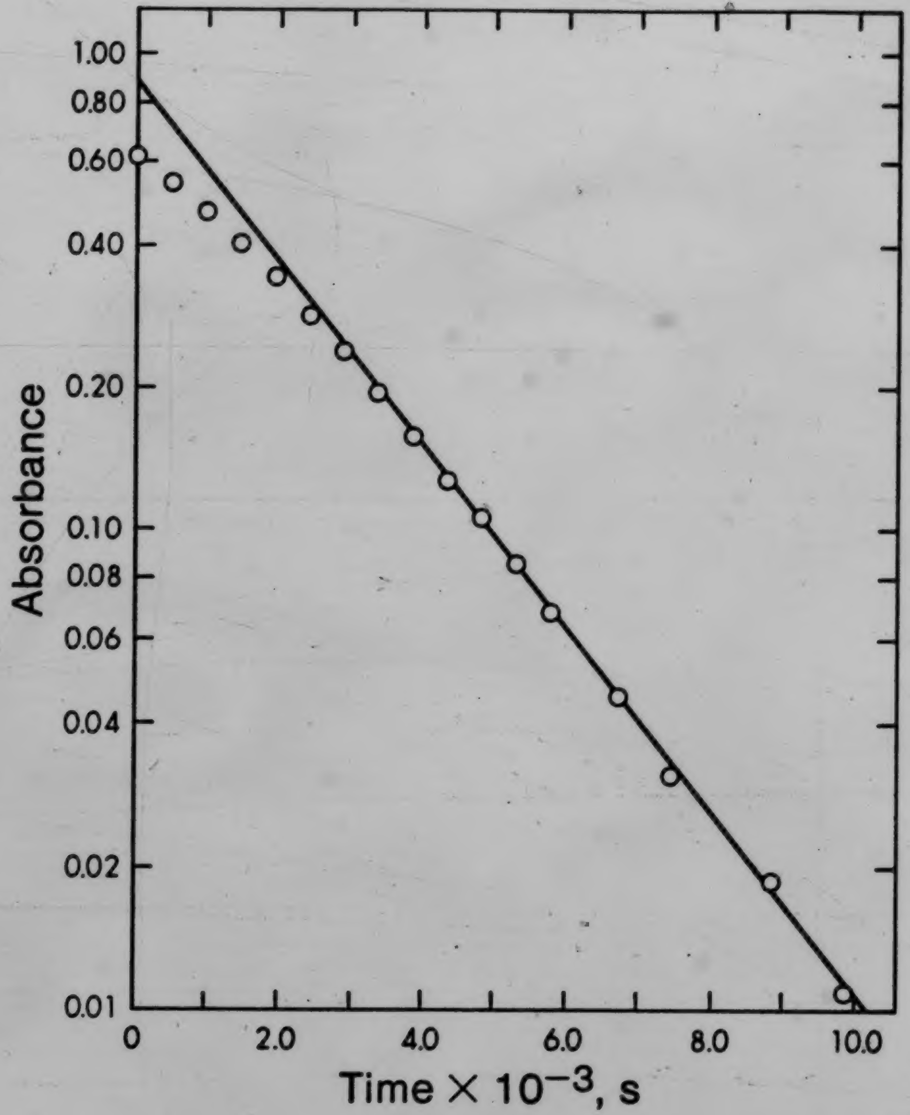


FIGURE 12. Semi-logarithmic plot of absorbance change *versus* time for the reaction of $(H_2O)_5CrCH(CN)CH_2CNCr(OH_2)_5{}^{5+}$ (6.40×10^{-4} M) with chromium(II) (6.06×10^{-2} M) at 408 nm; $[H^+]$ = 0.142 M; Ionic strength 0.50 M ($LiClO_4$); 25°C; 5 cm cell.

It is interesting to note that the chromium(II) independent term is identical with that observed for the uncatalyzed aquation of complex V-4. In any event, the results show that chromium(II) catalysis is a minor contributor to the aquation of complex V-4.

The pink complex (Band 4) formed in the reaction of chromium(II) with fumaronitrile could not be characterized since it could not be eluted from the Sephadex column. However, the decomposition products formed after allowing the column to stand at room temperature for two days could be collected by elution with 1 M $HClO_4$. The resulting solution was re-ion-exchanged on Dowex 50W-X2. Elution with 0.5 M $HClO_4$ effected separation of a red complex from a more strongly adsorbed blue complex. Chromate analysis indicated that equivalent amounts of chromium were present in both products and that the blue complex was $Cr(OH_2)_6^{3+}$. The red species had maxima at 519, 411 and 269 nm with extinction coefficients of 97.2, 128, and 3870 M^{-1} cm^{-1}, respectively, based on the chromium(III) content. Although the position of the band maxima are very similar to those for complex V-2, as shown in Figure 13, the extinction coefficients are significantly different, particularly at 519 nm. This hydrolysis product is tentatively assigned as either V-6 or V-7

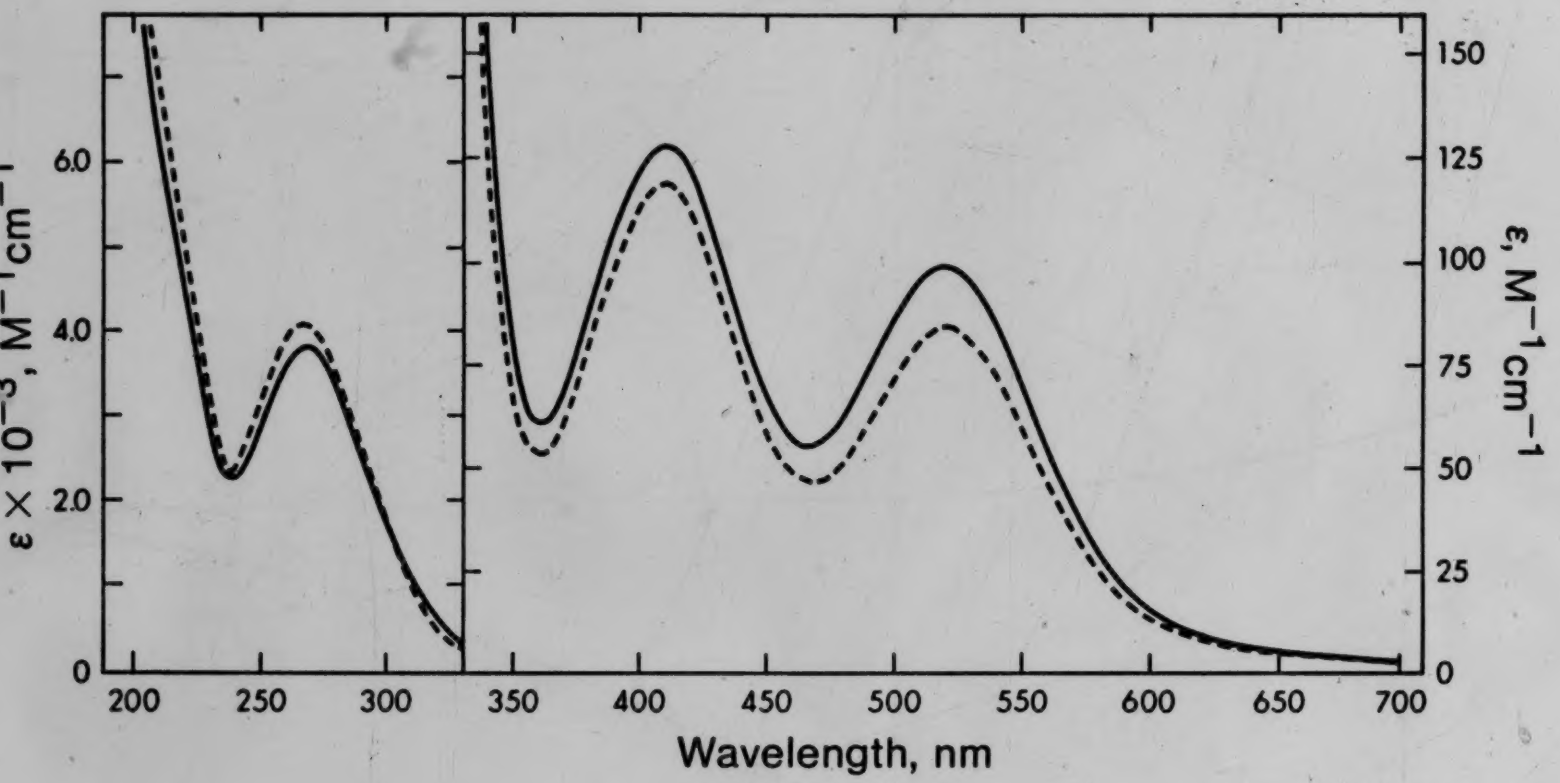
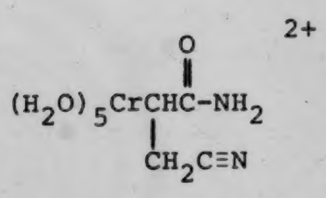
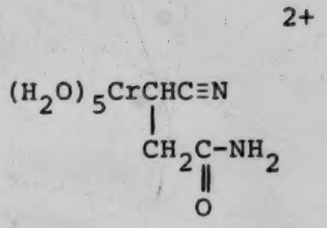


FIGURE 13. Electronic absorption spectra of complex V-6 (——) and $(H_2O)_5CrCH(CN)CH_2CN^{2+}$ (-----) at 25°C in 0.50 M $HClO_4$.



$(H_2O)_5CrCH(CH_2C{\equiv}N)C(=O)NH_2^{\;2+}$

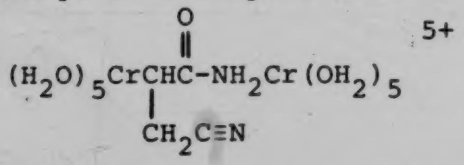
V-6



$(H_2O)_5CrCH(C{\equiv}N)CH_2C(=O)NH_2^{\;2+}$

V-7

where one of the nitrile groups has been hydrolyzed to give the corresponding carboxamide. However, the nature of the pink complex (Band 4) from which $Cr(OH_2)_6^{3+}$ and either V-6 or V-7 are formed is still uncertain since the charge of a complex such as V-8



$(H_2O)_5CrCH(CH_2C{\equiv}N)C(=O)NH_2Cr(OH_2)_5^{\;5+}$

V-8

or some other closely related complex, such as the oxygen-bonded carboxamide, does not seem consistent with the elution properties of this strongly retained complex.

The nature of the small amount of purple complex (Band 5) formed in the reduction of fumaronitrile is also uncertain. Unlike Band 4, no decomposition of this complex to elutable products is observed. As a result, even indirect characterization of Band 5 is not possible.

Detailed product studies were undertaken to ascertain the relative yields of the various chromium(III) complexes formed in the reduction of free fumaronitrile by chromium(II). It should be noted that the dichromium(III) complex V-4 is sufficiently unstable to aquation that during the time required to isolate this complex by ion-exchange, substantial amounts of V-4 are lost to aquation. However, as shown by equation (5.10), complex V-4 is quantitatively converted to complex V-2 and $Cr(OH_2)_6^{3+}$, so that if the reaction mixture is allowed to stand for sufficient periods to allow complete aquation of V-4, then the amount of V-2 isolated is an accurate measurement of the total amount of V-4 and V-2 produced originally by the reduction reaction. Therefore, the following procedure was employed. Solutions of fumaronitrile in acidic media were treated with chromium(II) and allowed to react for one or two half-times. Longer reaction times were not feasible since, as described earlier, the various products formed are subject to chromium(II) catalyzed decomposition. Excess chromium(II) was destroyed by oxidation with either $[(NH_3)_5CoN_3](ClO_4)_2$ or oxygen, and the resulting solutions were cooled quickly to 1°C and charged onto columns of Sephadex SP-C25. The initial eluent was collected and analyzed for unreacted fumaronitrile. The amount of fumaronitrile recovered provides a means by which the yields of the chromium(III) products can be determined. All complexes up to and including the dichromium complex V-4 were eluted as soon as possible from the column with 0.1 M $HClO_4$ in 0.9 M $NaClO_4$. This fraction was stored at room temperature for 5 hours, during which time complex V-4 completely aquates to $Cr(OH_2)_6^{3+}$ and complex V-2. The resulting solution was re-ion-exchanged on Dowex 50W-X2 and separated into the various bands by elution with perchloric acid solutions of increasing concentration. Each band was collected and analyzed for chromium. The remaining complexes on the Sephadex column were allowed to stand for 2 days at room temperature after which the hydrolyzed products were collected with 1 M $HClO_4$. Treatment of the small purple band (Band 5) at the top of the column with alkaline peroxide afforded an estimate of its relative yield. The results of this study are shown in Table 18. Values tabulated as "% as Chromium" were determined by comparing the amount of chromium(III) in the various bands to the total amount of chromium(III) products expected, assuming two equivalents of chromium(II) are consumed for each mole of NCCH=CHCN reduced, as was found in the stoichiometry experiments. The results clearly show that essentially complete recovery of chromium in the various products is obtained. This is further evidence in support of the stoichiometry results. In addition, the results reveal that most of the chromium(III) is found as $Cr(OH_2)_6^{3+}$. However, a large percentage of the latter arises from aquation of complex V-4. Therefore, it is more informative to examine the product distribution as a function of

Table 18

Distribution of Products in Reduction of NCCH=CHCN by Chromium(II).[a]

[H$^+$] M	Rx. Time, s	NCCH=CHCN consumed %[b]		Product Distribution, %				
				V-2	Cr(OH$_2$)$_6$$^{3+}$	Band 4	Band 5	Total
0.319	460	61.0	% as Chromium[c]	34.1	55.1	10.1	2.7	102.0
			% as Ligand[d]	68.2[e]	-	10.1[f]	2.7[f]	81.0
0.050	460	59.4	% as Chromium[c]	37.7	51.4	8.1	1.1	98.3
			% as Ligand[d]	75.4[e]	-	8.1[f]	1.1[f]	84.6

---

[a] Initial reactant concentrations: [NCCH=CHCN] = 1.65×10^{-2} M; [Cr^{2+}] = 3.80×10^{-2} M.

[b] Determined by analyzing initial eluant for unreacted NCCH=CHCN.

[c] Values obtained by determining chromium content of individual bands and comparing to the total yield of chromium(III) products expected, assuming stoichiometry of 2Cr(II):1NCCH=CHCN.

[d] Values calculated on basis of amount of fumaronitrile consumed.

[e] Based on the assignment that complex V-2 has chromium:ligand ratio of 1:1.

[f] Based on complexes having chromium:ligand ratio of 2:1.

the ligand present in the various complexes isolated. Values reported as "% as Ligand" were calculated on the basis of the known chromium(III) content of the various bands and by assuming that the ratio of Cr:Ligand for complex V-2 is 1:1, whereas for Bands 4 and 5, a ratio of 2:1 is assumed. The evidence for such an assignment for complex V-2 has already been described. There is some evidence to substantiate the 2:1 ratio for Band 4 since it is known to decompose to equivalent amounts of $Cr(OH_2)_6^{3+}$ and complex V-6. However, there is no independent evidence for Band 5 and as such, the 2:1 ratio of chromium:ligand is simply assumed. In any event, the results suggest that most of the reduced ligand is found in complex V-2, with much smaller amounts attributed to the complexes comprising Bands 4 and 5.

Two specific results should be noted. It appears that there is a modest increase (7.2%) in the yield of complex V-2 as the acidity is varied from 0.319 to 0.050 M $HClO_4$, at the expense of the other products formed. In addition, less than 85% of the ligand can be accounted for as organochromium(III) complexes.

Additional experiments were undertaken to determine whether all or only some of the complex V-2 observed in the previous study arises from aquation of complex V-4. Solutions at different acidities but identical in all other respects were allowed to react with chromium(II) for about one half-time. The solutions were then air-oxidized, quickly cooled in an ice-bath and then immediately ion-exchanged on Dowex 50W-X2 at 2°C. The initial eluant was collected and analyzed for unreacted fumaronitrile. The red complex V-2 was collected within one hour and its chromium content determined. The results are given in Table 19. Also shown in Table 19 are the yields of complex V-2 obtained in the previous study. By comparing the two sets of results it is clear that most of complex V-2 isolated in the previous experiment results from aquation of complex V-4, which is the principal product formed in the initial reduction reaction. The 8.5% yield of complex V-2 observed at the higher acidity is easily accounted for by the aquation of complex V-4 during the time required for isolation. Therefore, it is suggested that at the higher acidity, no complex V-2 is formed directly by the reduction reaction. However, at the lower acidity, 6.7% more of complex V-2 is observed. Since from previous studies it is known that the rate of decomposition of complex V-4 is unaffected by the acid concentration, this increase must arise from the initial reduction reaction itself. It is also interesting to note that this increase in the amount of complex V-2 is in good agreement with the 7.2% increase in complex V-2 observed in the earlier study on proceeding from high to low acid concentrations.

Table 19

Percentage $(H_2O)_5CrCH(CN)CH_2CN^{2+}$ Formed in Reduction of NCCH=CHCN by Chromium(II)

10^2x [NCCH=CHCN], M	10^2x $[Cr^{2+}]$, M	$[H^+]$, M	Rx. Time, s	NCCH=CHCN consumed, %[a]	V-2, %[b,c]
3.12	6.84	0.400	200	64.9	8.5(68.2)
3.12	6.84	0.067	200	64.4	15.2(75.4)

[a] Determined by analyzing initial eluant for unreacted fumaronitrile.

[b] Values represent the percentage of reduced ligand isolated as complex V-2.

[c] Values in parenthesis are taken from Table 18.

Shown in Table 20 is the product distribution of the initial reduction reaction after correcting for the aquation of complex V-4 to complex V-2 and $Cr(OH_2)_6^{3+}$. The entries in the table are obtained by comparing the results shown in Tables 18 and 19 and on the basis of the above discussion. In addition, it has been assumed that the different chromium(II) concentrations (0.0380 and 0.068 M) of the two studies affect only the rate and not the product distributions. Also, the high and low acid ranges examined in the two studies were not identical (0.400 versus 0.319 M, and 0.067 versus 0.050 M). However, it is unlikely that these small differences will appreciably effect the comparison. The results suggest that the yield of the principal product V-4 is unaffected by the acid concentration. It is also interesting to note that there is substantial formation of $Cr(OH_2)_6^{3+}$, even after correcting for the amount formed by aquation of complex V-4. In addition, it may be noteworthy that on proceeding from high to low acid concentrations, there is a decrease in the yield of $Cr(OH_2)_6^{3+}$ formed as a result of the reduction of fumaronitrile that is proportional to the increase in the yield of complex V-2. Finally, if it is assumed that the yields of $Cr(OH_2)_6^{3+}$ shown in Table 20 correspond to the amounts of succinonitrile formed in the reaction, then all of the reduced

Table 20

Product Distribution of Initial Reaction of NCCH=CHCN with Chromium(II)

	Product Distribution, %[a]					
	V-2[b]	V-4[c]	$Cr(OH_2)_6^{3+}$ [d]	Band 4[c]	Band 5[c]	Total
High Acid (0.400 to 0.319 M)	0	68.2	(21.1)	10.1	2.7	102.1
Low Acid (0.067 to 0.050 M)	6.7	68.7	(13.6)	8.1	1.1	98.2

[a] Product distributions are based on amount of ligand contained in the various fractions.

[b] Based on the assignment that complex V-2 has chromium:ligand ratio of 1:1.

[c] Based on the assumption that these complexes have chromium:ligand ratio of 2:1.

[d] Percentage of $Cr(OH_2)_6^{3+}$ remaining after accounting for aquation of complex V-4. Values reported are actually one-half the yield of $Cr(OH_2)_6^{3+}$ since stoichiometry results require that 2 moles of chromium(III) are formed for each mole of fumaronitrile reduced.

ligand is accounted for.

The biphasic kinetic traces obtained at 520 nm for the reduction of free fumaronitrile by chromium(II) were fitted by a non-linear least-squares procedure employing the consecutive reaction schemes

$$A \xrightarrow{k_1} B \xrightarrow{k_3} C \qquad (5.13)$$

and

$$A \xrightarrow{k_1'} B \xrightarrow{k_2'} C \xrightarrow{k_3'} D \qquad (5.14)$$

In the latter scheme, k_2' was held constant at the value $3.6 \times 10^{-4}\ s^{-1}$ which was the rate constant obtained for the aquation of complex V-4 . It should be noted, however, that substitution of this value of k_2' with the slightly larger values calculated for the aquation of complex V-4 in the presence of chromium(II) (equation 5.12) had little or no effect on the values obtained for k_1' in scheme (5.14). The values obtained for k_1 and k_1' are listed in Table C-18 of Appendix C. Regardless of whether scheme (5.13) or (5.14) is used, the first reaction (k_1 or k_1') exhibits a first order dependence on the fumaronitrile concentration and also appears to have an inverse acid dependency. However, the schemes differ in their dependency of the chromium(II) concentration. Shown in Figure 14 are plots of $k_1/[Cr^{2+}]$ and $k_1'/[Cr^{2+}]$ versus $[Cr^{2+}]$ at 0.100 M and 0.050 M $HClO_4$. The results obtained

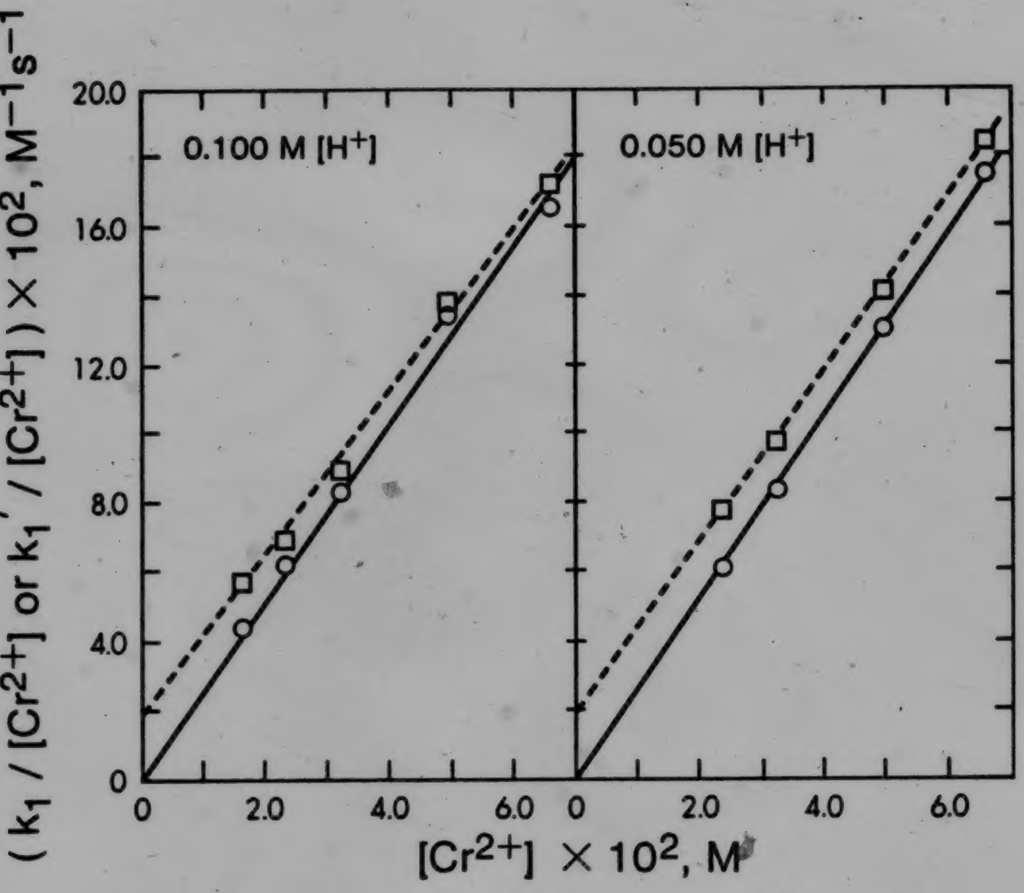


FIGURE 14. Variation of $k_1/[Cr^{2+}]$ (○) and $k_1'/[Cr^{2+}]$ (□) with $[Cr^{2+}]$ for the reduction of NCCH=CHCN at 25°C in 0.50 M $LiClO_4$-$HClO_4$ at 520 nm.

from scheme (5.13) suggest that the reduction is strictly second-order with respect to [Cr^{2+}] whereas the data, when fit to scheme (5.14) reveal an appreciable intercept, which suggests parallel first- and second-order chromium(II) dependent pathways. On this basis, scheme (5.13) suggests a rate law of the form

$$k_1 = \frac{a[Cr^{2+}]^2}{b + [H^+]} \tag{5.15}$$

where a = 2.5 ± 0.7 M^{-1} s^{-1} and b = (8.8 ± 0.3) x 10^{-1} M (25°C, 0.50 M $LiClO_4$-$HClO_4$). Alternatively, scheme (5.14) suggests a rate law of the type

$$k_1' = (a + \frac{b[Cr^{2+}]}{c + [H^+]})\ [Cr^{2+}] \tag{5.16}$$

where a = (1.9 ± 0.8) x 10^{-2} M^{-1} s^{-1}, b = (9.8 ± 3.4) x 10^{-1} M^{-1} s^{-1} and c = (3.4 ± 1.2) x 10^{-1} M. Of the two schemes examined, (5.14) seems somewhat more preferable since it takes into account the aquation of complex V-4 to complex V-2, which scheme (5.13) does not. However, we have not been able to devise a reasonable mechanism consistent with either rate law since both schemes suggest that the reduction is accelerated at low acid concentrations. This is a feature that is difficult to accommodate in a mechanism in which the reactants have no acid-base properties themselves and in which protons are actually consumed in the reduction. Indeed, some additional studies suggest that the reduction of fumaronitrile is actually independent of the acid concentration.

Product studies were undertaken in which mixtures of fumaronitrile and chromium(II) were allowed to react for various lengths of time. Reaction mixtures were then air-oxidized and charged onto ion-exchange columns. The unreacted fumaronitrile was collected in the initial eluant and the amount of the ligand consumed was determined. Assuming a simple third-order rate law for the disappearance of ligand, the general equation given in the Experimental Section (equation (5.3)) can be used to obtain values of the rate constant k. The values obtained are listed in Table 21. The results clearly show that the calculated third-order rate constant ($k = 3.5 \pm 0.4\ M^{-2}\ s^{-1}$) is independent of both the acid and chromium(II) concentrations. It should be noted, however, that the value for k is probably too large since reaction mixtures were quenched with O_2 which does not oxidize chromium(II) instantaneously, as was assumed in doing the calculations.

The discrepancy between the rate laws determined spectrophotometrically at 520 nm and by the quenching experiments is best rationalized by the assumption that during the reduction of fumaronitrile, an intermediate

Table 21

Rate Data for Reduction of NCCH=CHCN by Chromium(II) at 25°C

10^2x [NCCH=CHCN], M	10^2x [Cr^{2+}], M	[H^+], M	Rx. Time,[a] s	NCCH=CHCN consumed,[b] %	k,[c] M^{-2} s^{-1}
1.74	3.91	0.319	150	39.6	3.53
1.74	3.91	0.051	150	40.1	3.63
1.65	3.80	0.319	460	61.0	3.39
1.65	3.80	0.051	460	59.4	3.12
3.12	6.84	0.400	200	64.9	3.19
3.12	6.84	0.200	200	64.6	3.13
3.12	6.84	0.067	200	64.4	3.08
1.53	3.18	0.344	510	56.2	3.89
1.53	3.18	0.195	510	55.9	3.85
1.53	3.18	0.047	510	55.1	3.65

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[a] Values reported correspond to the time interval between injection of chromium(II) and subsequent air-oxidation.

[b] Determined by checking initial eluant for unreacted fumaronitrile.

[c] Calculated using equation (5.3).

species is formed which affects the spectrophotometric determination. Indeed, scan runs in the 330 to 485 nm region suggest the formation of just such a species. As shown in Figure 15, the absorbance throughout the region is observed to increase initially. However, over longer reaction times, the absorbance below 375 nm is observed to decrease while the maximum near 410 nm is still increasing in intensity. The nature of this intermediate species which absorbs below 375 nm and which undergoes decomposition is uncertain. However, it should be noted that it is more readily detected at higher acid and chromium(II) concentrations. In addition, preliminary results suggest that it may undergo more facile decomposition with decreasing acid concentrations.

As a further check on this system, the reduction reaction was monitored at 750 nm. At this wavelength, none of the organochromium(III) complexes exhibit any absorbance and any absorbance change observed should result solely from the loss of chromium(II) which does absorb at this wavelength ($\varepsilon = 4.5\ M^{-1}\ cm^{-1}$). Indeed, the anticipated absorbance decrease was observed and logarithmic plots of absorbance change versus time were linear to about four half-times. The kinetic data are summarized in Table C-19 of Appendix C. The results reveal that the rate of loss of chromium(II) is independent

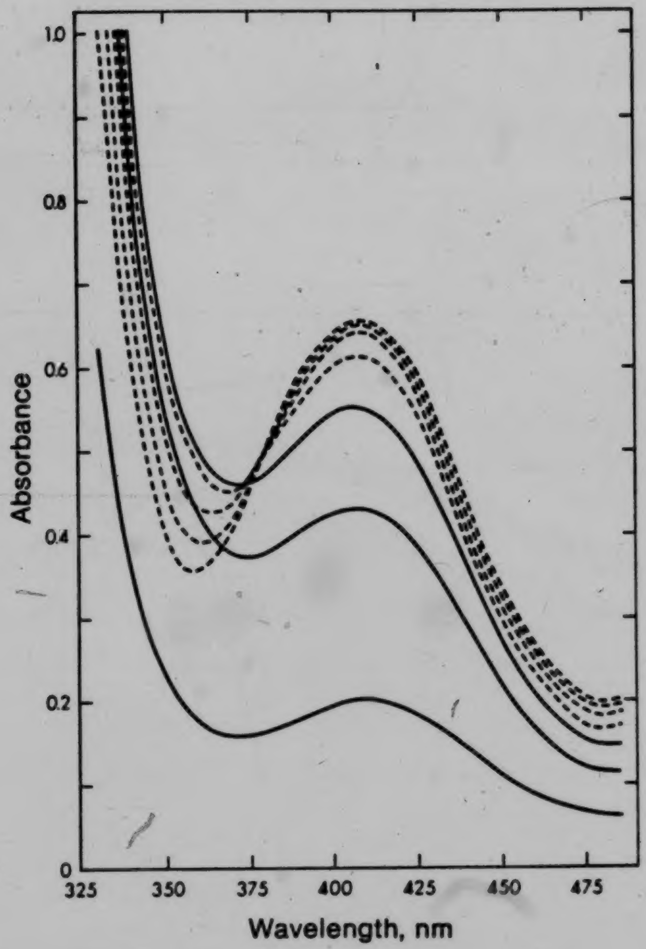


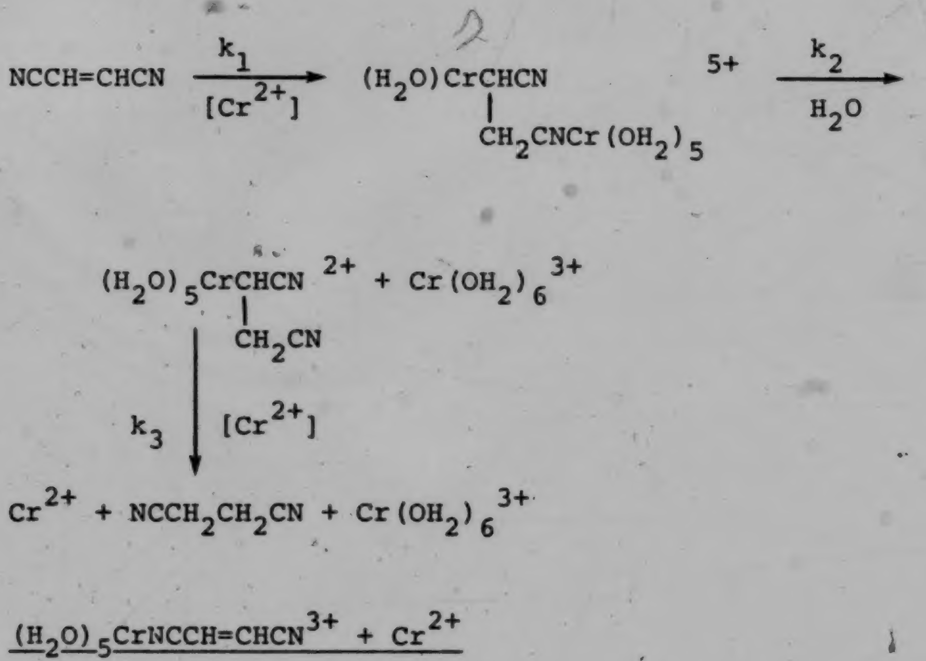
FIGURE 15. Absorbance changes in the 330 to 485 nm region during reduction of NCCH=CHCN (1.45×10^{-3} M) by chromium(II) (2.97×10^{-2} M) in 1.36 M $HClO_4$; 25°C; Ionic strength 1.50 M ($LiClO_4$); 5 cm cell. Spectral scans were at 2 minute intervals. The solid lines (———) represent scans for which the absorbance is increasing at all wavelengths. Dashed lines (-----) represent scans for which the absorbance is decreasing at wavelengths below 375 nm but still increasing in intensity above 375 nm.

of the acid concentration and is second-order with respect to the chromium(II) concentration, obeying the rate law

$$\frac{-d[Cr^{2+}]}{dt} = k[NCCH{=}CHCN][Cr^{2+}]^2 \qquad (5.17)$$

where k has the value 2.8 ± 0.3 M^{-2} s^{-1} (25°C, 0.50 M $LiClO_4$-$HClO_4$). The simple third-order behaviour observed at this wavelength serves to corroborate the earlier suggestion that an absorbing intermediate affects the rate law determination at 520 nm.

Although the proposed absorbing intermediate has affected the absorbance data at 520 nm with respect to the first phase of the reaction between chromium(II) and fumaronitrile, it is possible that either scheme (5.13) or (5.14) may adequately describe the last phase of the reaction. This is thought to correspond to the chromium(II) catalyzed aquation of the organochromium(III) products formed. The values obtained for k_3 and k_3' are tabulated in Table C-20. It is worth noting that the second-order rate constant k_3 (M^{-1} s^{-1}) obtained from scheme (5.13) increases with decreasing chromium(II) concentrations. On the other hand, values for k_3' (M^{-1} s^{-1}) obtained using scheme (5.14) are relatively constant with varying reductant concentrations, although the magnitude of k_3' increases moderately with decreasing acid concentrations. This is probably a residual effect of the absorbing intermediate. In any event, the average value of k_3' (ca. 0.011 $M^{-1}\ s^{-1}$) agrees quite closely with the value of 0.0119 $M^{-1}\ s^{-1}$ obtained earlier for the chromium(II) catalyzed aquation of complex V-2 (Table C-15). Therefore, on the basis of the product studies already described and the kinetic studies presented here, the principal reaction scheme for the reaction between fumaronitrile and chromium(II) can be formulated as



$$\mathrm{NCCH{=}CHCN} \xrightarrow[{[Cr^{2+}]}]{k_1} \Big[\mathrm{(H_2O)Cr}\underset{\substack{|\\ \mathrm{CH_2CNCr(OH_2)_5}}}{\mathrm{CH}}\mathrm{CN}\Big]^{5+} \xrightarrow[H_2O]{k_2}$$

$$\Big[\mathrm{(H_2O)_5Cr}\underset{\substack{|\\ \mathrm{CH_2CN}}}{\mathrm{CH}}\mathrm{CN}\Big]^{2+} + \mathrm{Cr(OH_2)_6}^{3+}$$

$$\Big\downarrow k_3\ [Cr^{2+}]$$

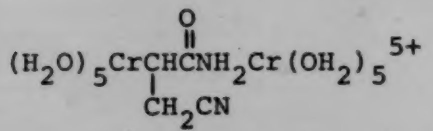
$$\mathrm{Cr^{2+} + NCCH_2CH_2CN + Cr(OH_2)_6}^{3+} \qquad (5.18)$$

$$\underline{\mathrm{(H_2O)_5CrNCCH{=}CHCN^{3+} + Cr^{2+}}}$$

Significantly different results are obtained when chromium(II) is allowed to react with complex V-1, $(H_2O)_5CrNCCH{=}CHCN^{3+}$, which is the initial product formed by reaction of chromium(II) with $(NH_3)_5CoNCCH{=}CHCN^{3+}$. In the product studies, the reaction was allowed to proceed for ten half-times and then excess chromium(II) was oxidized with either O_2 or $[(NH_3)_5CoN_3](ClO_4)_2$. Both oxidants were employed in separate ion-exchange experiments since their reduction products, $[(H_2O)_4Cr(OH)]_2^{4+}$ and $(H_2O)_5CrN_3^{2+}$, respectively, have considerably different elution properties that allow the successful isolation of all the products formed by reduction of complex V-1. Reaction mixtures were charged onto columns of Sephadex SP-C25 cation-exchange resin and the initial eluant was collected and analyzed for any unreduced fumaronitrile ligand. By combining the results obtained from the two different oxidants, the following observations were made. A red fraction (Band 1') was eluted from the column with 0.2 M $HClO_4$. This fraction was found to consist of a small amount of a chromium-containing species as well as large amounts of Co^{2+}, the latter formed from the reduction of the cobalt(III) complex. Complete characterization of the chromium(III) complex by electronic absorption was not possible due to its low yield and extensive contamination with Co^{2+}. However, the complex appears to have maxima in the 520, 410 and 270 nm regions. This, coupled with its elution properties, allows the complex to be tentatively formulated as complex V-2, $(H_2O)_5CrCH(CN)CH_2CN^{2+}$, which is also a product from the reduction of free fumaronitrile.

A blue band (Band 2') was eluted from the column with 0.2 M $HClO_4$ in 0.2 M $NaClO_4$. Characterization of this fraction revealed that it was $Cr(OH_2)_6^{3+}$. More strongly retained on the column was a small, yellow-red fraction (Band 3') which was removed from the column using 0.2 M $HClO_4$ in 0.5 M $NaClO_4$. Analysis on representative samples of this fraction revealed that it contained both a cobalt(III) complex and a chromium-containing species. The cobalt(III) complex is presumably $(NH_3)_5CoNH_2C(O)CH{=}CHCN^{3+}$ which, from independent studies,[151] is known to be formed by hydrolysis of the cobalt(III) complex of fumaronitrile. Again, because of this contamination and the low yield of the chromium complex, the complex was not characterized by its electronic spectrum. Nevertheless, its elution properties are identical with those observed for complex V-4 which is also formed in the reduction of free fumaronitrile, and is assigned as such.

A purple band (Band 4') was eluted from the column with 0.2 M $HClO_4$ in 0.8 M $NaClO_4$. Its elution properties are similar to that of complex V-4 and is probably of similar charge. The electronic spectrum of this complex revealed maxima at 532, 408 and 263 nm and, assuming that it is a dichromium(III) species, the molar extinction coefficients are calculated to be 116, 123 and 4782 M^{-1} cm^{-1}, respectively. Such a spectrum is consistent with an organochromium(III) species, and it is suggested that the complex can be formulated as

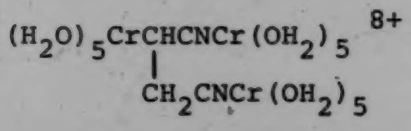


$$(H_2O)_5Cr\underset{\substack{|\\ CH_2CN}}{C}H\overset{\substack{O\\ \|}}{C}NH_2Cr(OH_2)_5^{\ 5+}$$

V-8

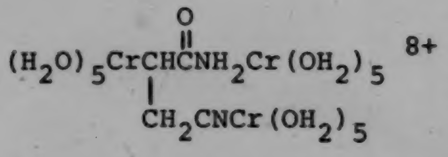
where the coordinated nitrile has been hydrolyzed to the corresponding carboxamide. As illustrated, complex V-8 is assigned as the nitrogen-coordinated isomer, although it is possible that linkage isomerization to the oxygen-bonded carboxamide has occured.

A strongly retained red-purple fraction (Band 5') was eluted from the Sephadex column with 1 M $HClO_4$ in 2 M $NaClO_4$. The strong binding to the resin suggests that it is highly charged and is probably a trichromium(III) species. Its electronic spectrum is shown in Figure 16 and exhibits maxima at 529, 405 and 260 nm with molar extinction coefficients of 155, 145 and 6540 M^{-1} cm^{-1}, respectively. This complex may be formulated as either V-9 or V-10.



$$(H_2O)_5Cr\underset{\substack{|\\ CH_2CNCr(OH_2)_5}}{C}HCNCr(OH_2)_5^{\ 8+}$$

V-9



$$(H_2O)_5Cr\underset{\substack{|\\ CH_2CNCr(OH_2)_5}}{C}H\overset{\substack{O\\ \|}}{C}NH_2Cr(OH_2)_5^{\ 8+}$$

V-10

In structure V-10, the nitrile group adjacent to the organochromium(III) moiety has been hydrolyzed. As for

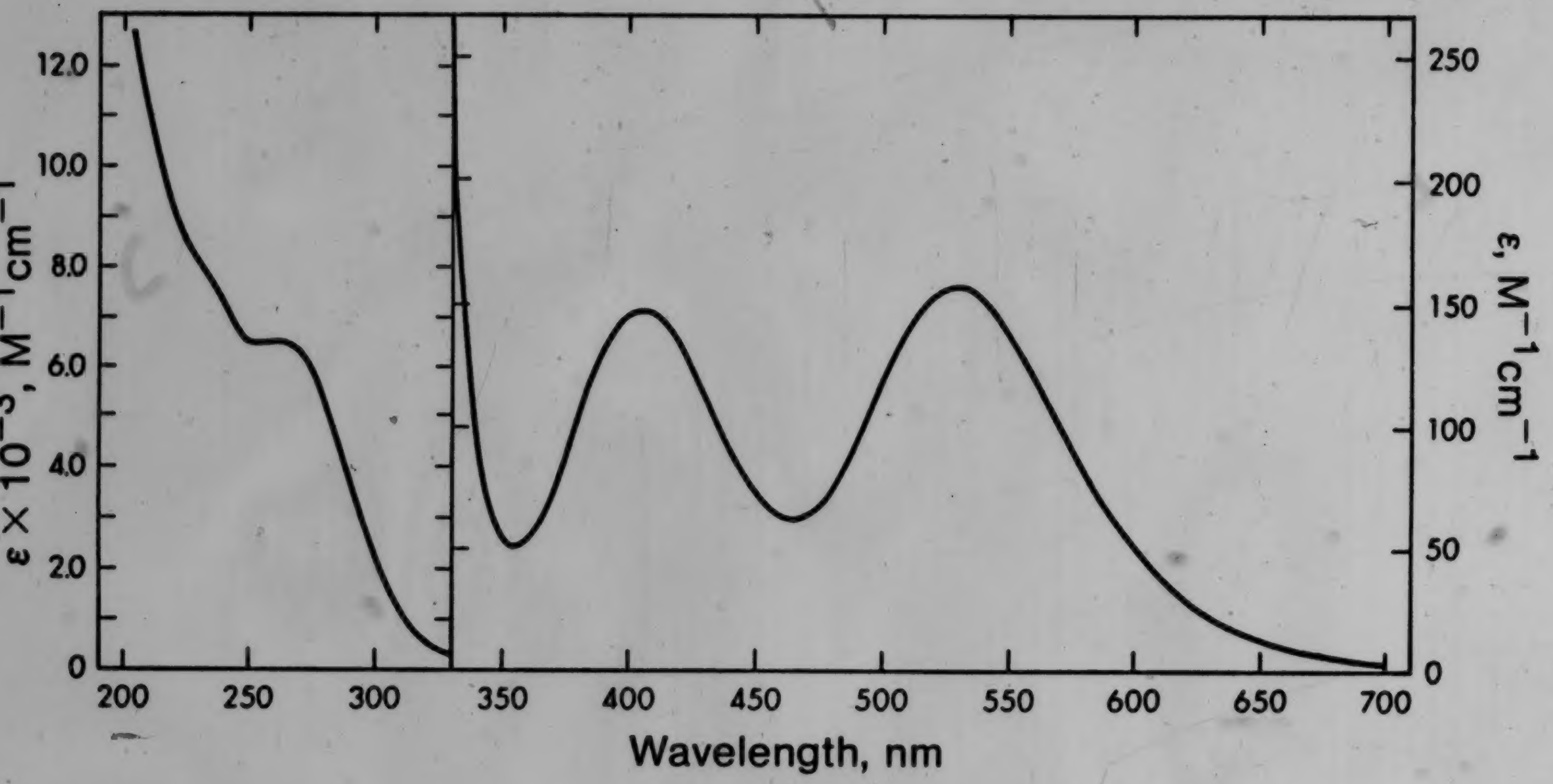
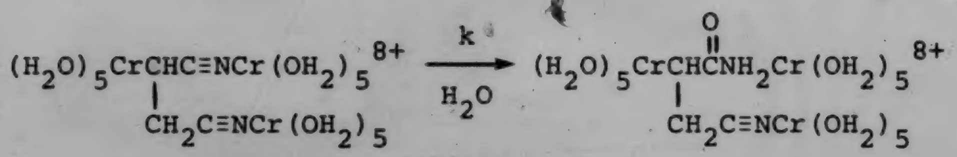


FIGURE 16. Electronic absorption spectrum of complex V-10 in 1 M $HClO_4$ and 2 M $NaClO_4$ at 25°C.

complex V-8, isomerization to the oxygen-bonded carboxamide complex is possible.

These possibilities may be distinguished on the basis of other information. Certainly, of the two species shown, V-9 would be the more likely initial product of the reaction between V-1 and chromium(II). However, immediately following the initial reduction reaction, a second rapid reaction was observed at 355 and 750 nm. The rate of this reaction was found to be independent of both the acid and chromium(II) concentrations. The rate data for this reaction are summarized in Table C-21 of Appendix C. The first-order rate constant was found to be 0.103 ± 0.010 s^{-1} (25°C, 0.50 M $LiClO_4$-$HClO_4$) and it may correspond to the hydrolysis of V-9, according to the reaction

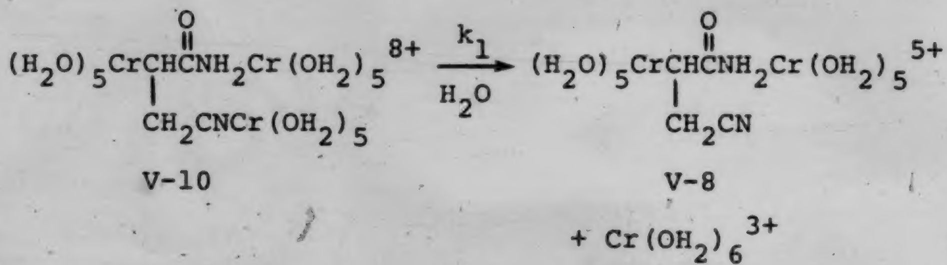


$$\begin{array}{l}(H_2O)_5CrCHC{\equiv}NCr(OH_2)_5^{\,8+}\\ \qquad\quad |\\ \qquad\quad CH_2C{\equiv}NCr(OH_2)_5\end{array} \xrightarrow[H_2O]{k} \begin{array}{l}\qquad\qquad\quad\;\; O\\ \qquad\qquad\quad\;\; \|\\ (H_2O)_5CrCHCNH_2Cr(OH_2)_5^{\,8+}\\ \qquad\quad |\\ \qquad\quad CH_2C{\equiv}NCr(OH_2)_5\end{array} \qquad (5.19)$$

V-9 V-10

Therefore, the complex isolated by ion-exchange chromatography is believed to be V-10, or its oxygen-bonded isomer.

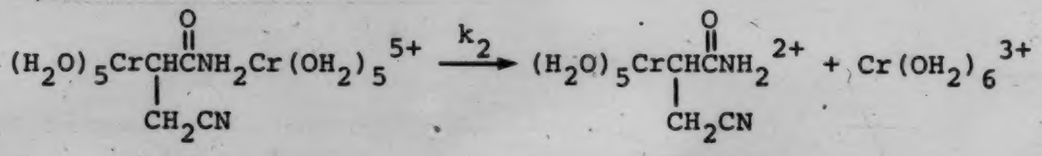
In aqueous acid, this proposed trimetallic species is observed to undergo spectral changes. In the ultraviolet region, the shoulder at 235 nm disappears and an isosbestic point is maintained at 308 nm. In the visible region, the absorbance decreases in the 530 nm region whereas a small increase is observed near 410 nm, as shown in Figure 17. The maximum at 529 nm shifts initially to 532 nm after four hours, during which time isosbestic behaviour is found at 444 and 406 nm. This low energy band subsequently shifts slowly to 522 nm with an isosbestic point at 498 nm. These spectral changes suggest two consecutive reactions. The initial changes in the visible spectrum are consistent with the formation of V-8 which, at least for the present series of organochromium(III) complexes, is unique in the position of its low-energy absorption band (λ_{max} = 532 nm).



$$(H_2O)_5Cr\underset{|\atop CH_2CNCr(OH_2)_5}{CH}\overset{O}{\overset{\|}{C}}NH_2Cr(OH_2)_5{}^{8+} \xrightarrow[H_2O]{k_1} (H_2O)_5Cr\underset{|\atop CH_2CN}{CH}\overset{O}{\overset{\|}{C}}NH_2Cr(OH_2)_5{}^{5+} + Cr(OH_2)_6{}^{3+} \quad (5.20)$$

V-10 → V-8

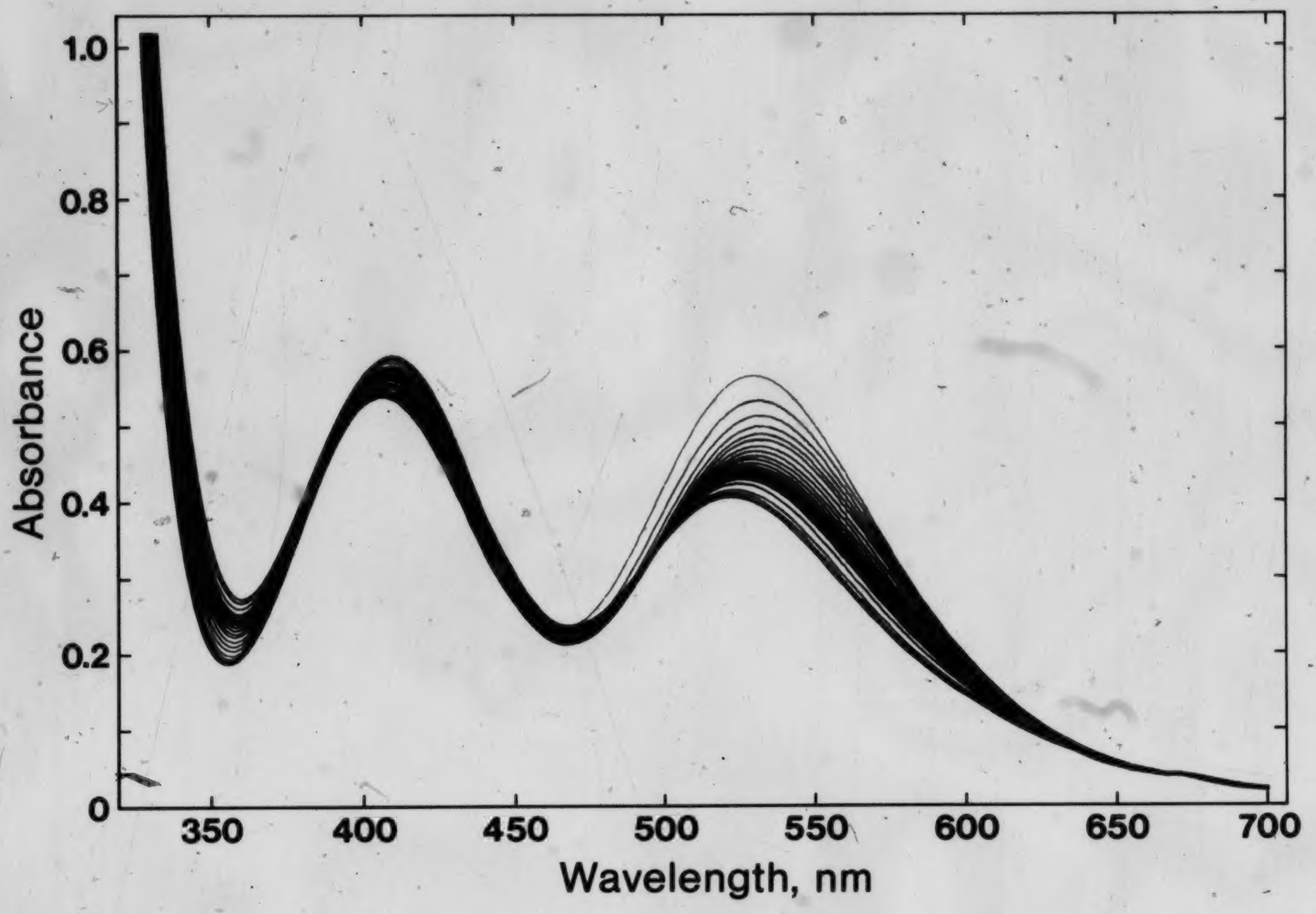
The second phase of the reaction probably corresponds to the aquation reaction



$$(H_2O)_5Cr\underset{|\atop CH_2CN}{CH}\overset{O}{\overset{\|}{C}}NH_2Cr(OH_2)_5{}^{5+} \xrightarrow{k_2} (H_2O)_5Cr\underset{|\atop CH_2CN}{CH}\overset{O}{\overset{\|}{C}}NH_2{}^{2+} + Cr(OH_2)_6{}^{3+} \quad (5.21)$$

V-8 → V-6

FIGURE 17. Changes in the visible spectrum during aquation of complex V-10 (7.33×10^{-4} M) in 1 M $HClO_4$ and 2 M $NaClO_4$ at 25°C; 5 cm cell. Spectral scan runs were recorded at 0, 1, 2, 3, 4, 5, 6.5, 8, 9.5, 11, 12.5, 14, 15.5, 17, 18.5, 20, 21.5, 23, 30, 42, 50, 58 and 64 hours after isolation by ion-exhcange chromatography. The absorbance near 530 nm is decreasing with time while the maximum near 410 nm is increasing in intensity.



Absorbance
1.0
0.8
0.6
0.4
0.2
0
350
400
450
500
550
600
650
700
Wavelength, nm

Indeed, when the reaction is monitored at 240 nm, the absorbance changes fit a consecutive reacton scheme. For [V-10] = 1.4×10^{-4} M, [$HClO_4$] = 0.10 M and [$NaClO_4$] = 0.10 M, non-linear least-squares analysis of the absorbance changes yield $k_1 = 2.0 \times 10^{-4}\ s^{-1}$ and $k_2 = 3.6 \times 10^{-5}\ s^{-1}$ at 25°C.

Product analysis experiments on Dowex 50W-X2 of hydrolyzed mixtures of complex V-10 corroborate the reactions described above. Elution with 0.5 M $HClO_4$ separated a red complex from a more strongly adsorbed blue species which was eluted with 1.0 M $HClO_4$. Chromate analysis revealed that the ratio of the chromium content of complex V-10 : red band : blue band was 3.00:0.96 ± 0.04: 2.05 ± 0.03. The blue complex was determined to be $Cr(OH_2)_6^{3+}$ from its spectral properties. The red fraction has maxima at 518, 411 and 269 nm with extinction coefficients of 96.7, 125 and 3800 $M^{-1}\ cm^{-1}$, respectively. These spectral results are essentially identical with those reported previously for complex V-6 which is formed by hydrolysis of Band 4 obtained in the reduction of free fumaronitrile. Therefore, the chromium content, elution properties, and spectra of the final products substantiate equations (5.20) and (5.21).

The last product found in the reduction of complex V-1 is a purple species (Band 6') which does not elute from the column with even 1 M $HClO_4$ in 4 M $NaClO_4$. In addition, this complex does not decompose to elutable products. It could only be removed from the resin after conversion to chromate using alkaline peroxide.

Listed in Table 22 are the distributions of the products formed by the chromium(II) reduction of $(NH_3)_5CoNCCH{=}CHCN^{3+}$ at both 0.388 M and 0.05 M $HClO_4$. Values reported as "% as Chromium" were obtained by assuming that reduction of the cobalt(III) centre yielded one equivalent of chromium(III) in the form of complex V-1, which has already been demonstrated, and that the fraction of complex V-1 that undergoes additional reduction (as compared to aquation) consumes two additional equivalents of chromium(II). The results suggest that there is quantitative recovery of chromium in the various bands. Values reported as "% as Ligand" are based on the amount of fumaronitrile consumed, the amount of chromium found in the various bands, and the assumption that the products have the empirical formulae described above and as listed in Table 22. Clearly, complex V-10 is the principal product of the reduction. Indeed, the yield of V-10 may be larger than shown since it is likely that the small amounts of complex V-8 isolated arise from aquation of complex V-10 during the ion-exchange procedure. In addition, only marginal differences in the product distributions are observed at the two acid concentrations. It is also interesting to note that if

Table 22

Distribution of Products From Reduction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$ by Chromium(II).[a]

$[H^+]$, M	Rx. Time, s	V-1 consumed, %[b]		Product Distribution, %						
				V-2	V-4	$Cr(OH_2)_6{}^{3+}$	V-8	V-10	Band 6'	Total
0.388	120	94.4	% as Chromium[c]	0.5	2.3	11.0	7.5	67.8	9.7	98.8
			% as Ligand[d]	1.5[e]	3.6[f]	-	11.5[f]	69.2[g]	14.9[f]	100.7
									9.9[g]	95.7
0.050	120	88.8	% as Chromium	0.7	4.3	12.7	6.2	63.2	9.1	96.2
			% as Ligand[d]	2.2[e]	6.8[f]	-	9.7[f]	65.9[g]	14.2[f]	98.8
									9.5[g]	94.1

[a] Initial reactant concentrations: $[(NH_3)_5CoNCCH{=}CHCN^{3+}] = 3.90\times10^{-3}$ M; $[Cr^{2+}] = 2.03\times10^{-2}$ M.

[b] Determined by analyzing initial eluant for unreduced fumaronitrile.

[c] Values obtained by determining chromium content of individual bands and comparing to the total yield of chromium products expected, assuming one equivalent of chromium(III) is formed in the reduction of the cobalt(III) complex and two equivalents of chromium(III) are produced for each equivalent of V-1 that is reduced.

[d] Values calculated on basis of amount of V-1 consumed.

[e] Based on the assumption that complex V-2 has chromium:ligand ratio of 1:1.

[f] Assuming complex has chromium:ligand ratio of 2:1.

[g] Assuming complex has chromium:ligand ratio of 3:1.

the ratio of the chromium:ligand content of Band 6' is either 2:1 or 3:1, then essentially complete recovery of the ligand in the form of organochromium(III) complexes is observed. This differs from the reduction of free fumaronitrile where less than 85% of the ligand is found coordinated to chromium(III). Also, the yield of $Cr(OH_2)_6^{3+}$ in the present study is smaller and is readily accounted for by partial aquation of the various products formed.

The results of the kinetic investigations at 520 nm of the reduction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$, V-1, by chromium(II) are shown graphically in Figure 18. As illustrated, the pseudo-first-order rate constant (k_{obsd}) increases with decreasing acid concentrations and is also observed to increase with increasing chromium(II). However, the dependence on reductant concentration is not a simple one since both first- and second-order terms seem to be present. In light of the results obtained for the reduction of uncomplexed fumaronitrile, it is uncertain whether the complicated rate law is a true reflection of the mechanism of reduction of complex V-1, or whether, as for free fumaronitrile, it arises from the formation of an absorbing intermediate. Unfortunately, the reaction is too rapid to carry out quenching experiments to ascertain the extent of reduction of complex V-1 as a function of acid and chromium(II) concentrations. Such

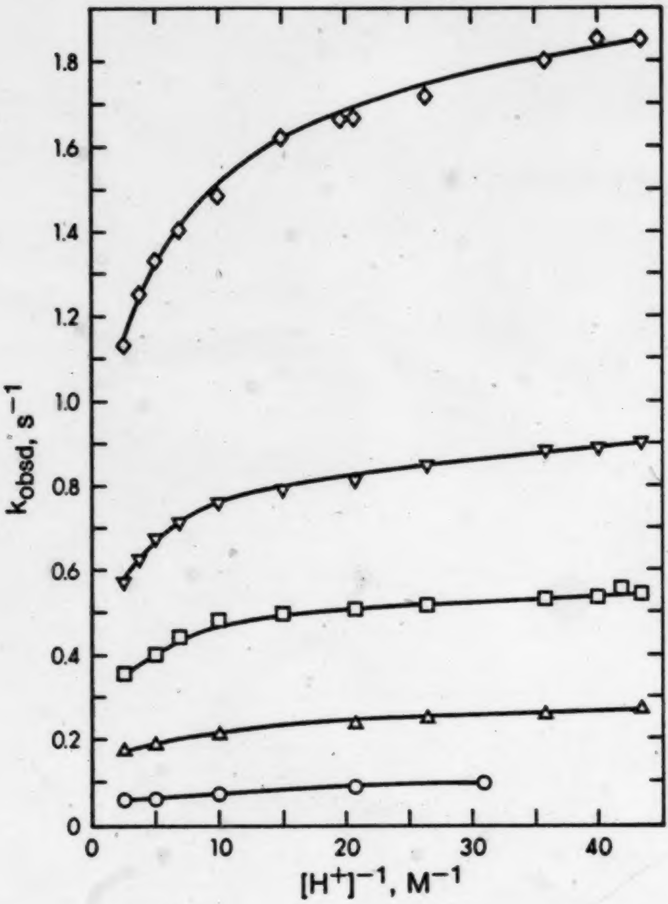


FIGURE 18. Variation of k_{obsd} with $[H^+]^{-1}$ for the reduction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$ by chromium(II) in 0.50 M $LiClO_4$-$HClO_4$ at 25°C; (○) 4.8×10^{-3} M $[Cr^{2+}]$; (△) 9.5×10^{-3} M $[Cr^{2+}]$; (□) 1.46×10^{-2} M $[Cr^{2+}]$; (▽) 1.94×10^{-2} M $[Cr^{2+}]$; (◇) 2.96×10^{-2} M $[Cr^{2+}]$.

experiments would have readily discerned between the two possibilities.

If the complicated rate data for the reaction, given in Table C-22 of Appendix C, are considered to arise from the formation of an absorbing intermediate, then devising a rate law consistent with the data is hardly justified. Indeed, although in qualitative agreement with the results at 520 nm, the results obtained at 410 and 750 nm are sufficiently different as to suggest that the kinetic data is wavelength dependent, at least at high chromium(II) and acid concentrations. In fact, at the latter wavelength, an absorbance increase is observed instead of the expected absorbance decrease. In addition, at high chromium(II) concentrations, logarithmic plots of absorbance change *versus* time deviated from linearity for up to the first 25% of the reaction, particularly at 410 nm. In any event, the results at 520 nm seem to be the most reliable and will be used in formulating the rate law for this reaction.

Also shown in Table C-22 of Appendix C are the values of k_{obsd} for this reaction which have been corrected (k_{obsd}^{corr}) for the aquation of complex V-1, which has already been described (equation (5.7)). It should be noted that this correction is only significant at lower chromium(II) concentrations where reduction and aquation of complex V-1 become competitive. The rate data at 520 nm are consistent with a rate law of the form

$$k_{obsd}^{corr} = \frac{(a/[H^+] + b[Cr^{2+}])[Cr^{2+}]}{1 + c[H^+][Cr^{2+}]} \quad . \qquad (5.22)$$

Non-linear least-squares analysis of the data to this scheme yields the values $a = (1.7 \pm 0.5) \times 10^{-1}\ s^{-1}$, $b = (2.01 \pm 0.12) \times 10^{3}\ M^{-2}\ s^{-1}$, and $c = (5.5 \pm 1.5) \times 10^{1}\ M^{-2}$ (25°C, 0.50 M $LiClO_4$-$HClO_4$). The calculated and observed rate constants are in good agreement, as is shown in Table C-22 of Appendix C. Other empirical rate laws were fitted to the data but none showed as good agreement between calculated and experimental values of k_{obsd}^{corr}.

Discussion

A summary of the kinetic parameters for the various reactions studied in this chapter are given in Table 23.

The reduction of $(NH_3)_5CoNCCH{=}CHCN^{3+}$ by chromium(II) is certainly a very facile process ($k = 1.9 \times 10^5\ M^{-1}\ s^{-1}$) and this suggests an inner-sphere mechanism of reduction of the type

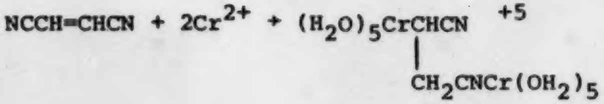
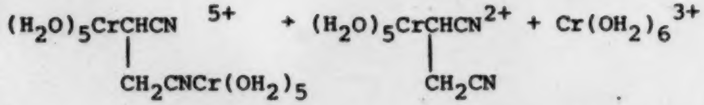
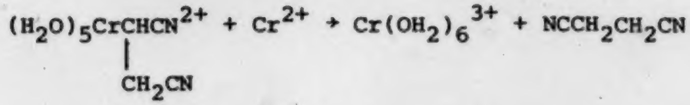
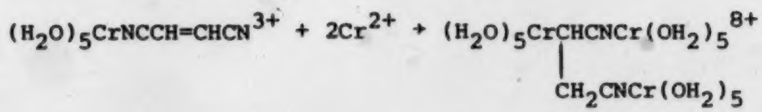
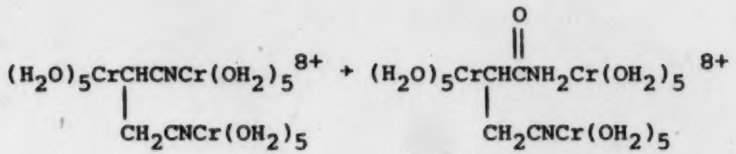
$$(NH_3)_5CoNCCH{=}CHCN^{3+} + Cr^{2+} \xrightarrow{k} 5NH_3 + Co^{2+} + \underset{\text{V-1}}{(H_2O)_5CrNCCH{=}CHCN^{3+}} \qquad (5.23)$$

Outer-sphere reductions of simple nitrile complexes of $(NH_3)_5Co^{3+}$ proceed with much smaller rate constants ($k \simeq 0.02 - 0.04\ M^{-1}\ s^{-1}$),[142] as noted in Chapter III. In addition, the detection of an intermediate which absorbs near 395 nm is convincing evidence supporting the proposed reaction scheme. Finally, the 1000-fold greater reactivity towards chromium(II) of V-1 as compared to free fumaronitrile shows that the latter is not produced in the reduction of $(NH_3)_5CoNCCH{=}CHCN^{3+}$.

It has been suggested[21,137] that cobalt(III) complexes containing reducible ligands may undergo reduction by a chemical mechanism in which a ligand-centred radical is initially formed which subsequently reduces the cobalt(III) oxidizing centre. Such a mechanism has been

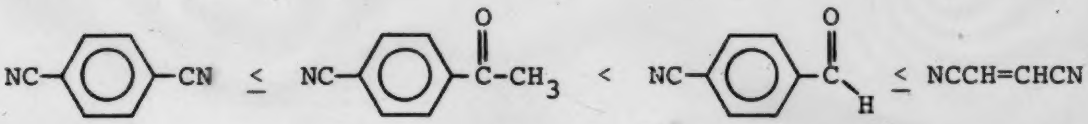
Table 23

Summary of Kinetic Parameters for Complexes Derived from Fumaronitrile

Reaction[a]	k
$(NH_3)_5CoNCCH{=}CHCN^{3+} \rightarrow 5NH_3 + Co^{2+} + (H_2O)_5CrNCCH{=}CHCN^{3+}$	$1.9\times10^{5}\ (M^{-1}\ s^{-1})$
$(H_2O)_5CrNCCH{=}CHCN^{3+} \rightarrow Cr(OH_2)_6{}^{3+} + NCCH{=}CHCN$	$1.19\times10^{-2} + \frac{4.14\times10^{-4}}{[H^+]}\ (s^{-1})$
 $NCCH{=}CHCN + 2Cr^{2+} \rightarrow (H_2O)_5Cr\underset{\substack{\vert \\ CH_2CNCr(OH_2)_5}}{C}HCN^{+5}$	$2.8\ (M^{-2}\ s^{-1})$
 $(H_2O)_5Cr\underset{\substack{\vert \\ CH_2CNCr(OH_2)_5}}{C}HCN^{5+} \rightarrow (H_2O)_5Cr\underset{\substack{\vert \\ CH_2CN}}{C}HCN^{2+} + Cr(OH_2)_6{}^{3+}$	$3.6\times10^{-4}\ (s^{-1})$
 $(H_2O)_5Cr\underset{\substack{\vert \\ CH_2CN}}{C}HCN^{2+} + Cr^{2+} \rightarrow Cr(OH_2)_6{}^{3+} + NCCH_2CH_2CN$	$1.19\times10^{-2}\ (M^{-1}\ s^{-1})$
 $(H_2O)_5CrNCCH{=}CHCN^{3+} + 2Cr^{2+} \rightarrow (H_2O)_5Cr\underset{\substack{\vert \\ CH_2CNCr(OH_2)_5}}{C}HCNCr(OH_2)_5{}^{8+}$	$\dfrac{\left(\frac{0.17}{[H^+]} + 2.01\times10^{3}[Cr^{2+}]\right)[Cr^{2+}]}{1 + 55[H^+](Cr^{2+}]}\ (s^{-1})$
 $(H_2O)_5Cr\underset{\substack{\vert \\ CH_2CNCr(OH_2)_5}}{C}HCNCr(OH_2)_5{}^{8+} \rightarrow (H_2O)_5Cr\underset{\substack{\vert \\ CH_2CNCr(OH_2)_5}}{C}H\overset{\substack{O \\ \Vert}}{C}NH_2Cr(OH_2)_5{}^{8+}$	$0.103\ (s^{-1})$

[a] Ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

proposed for several systems, including the complexes of isonicotinamide,[24] fumaric acid[48,139,152] and maleic acid.[140] It is thought that the rates of electron transfer may be related to the energy of the lowest unoccupied orbital on the ligand.[21,137] The energy of this orbital has been shown to be related to the polarographic half-wave reduction potential.[153] Shown below are a series of nitrile ligands which are listed in order of increasing ease of reducibility as judged from their polarographic half-wave reduction potentials,[142,149,154] and the rate constants for reductions of these $(NH_3)_5Co^{3+}$ complexes by chromium(II).



0.92 $M^{-1}\ s^{-1}$ (155)

6.0×10^3 $M^{-1}\ s^{-1}$ (142)

2.5×10^5 $M^{-1}\ s^{-1}$ (142)

1.9×10^5 $M^{-1}\ s^{-1}$

The results do show a qualitative relationship between ease of reducibility and rate of reduction but the nature of the reductant binding site also seems to be important. Therefore, the relative rates of the 4-formylbenzonitrile and fumaronitrile complexes compared to the terephthalonitrile and 4-acetylbenzonitrile complexes can be ascribed to their greater reducibility. However, the greater reduction rates for the 4-acetyl and 4-formyl derivatives compared to the nitriles of similar reducibility, terephthalonitrile and fumaronitrile, respectively, may be due to the greater Lewis basicity of the carbonyl oxygen compared to the nitrile nitrogen toward chromium(II).[156] In any event, the fact that the fumaronitrile complex fits the pattern just described and the observation that free fumaronitrile also undergoes net reduction by chromium(II) may suggest that reduction of $(NH_3)_5CoNCCH{=}CHCN^{3+}$ proceeds through a chemical mechanism.

The aquation of $(H_2O)_5CrNCCH{=}CHCN^{3+}$ is similar to many other $(H_2O)_5Cr^{III}X$ systems[84,157-160] in that it exhibits both an acid independent and inverse acid dependent term in the rate law. The inverse acid term is normally ascribed to reduction of

$$(H_2O)_4(HO)Cr^{III}X \ .$$

Some representative examples are shown in Table 24. However, complex V-1 differs from other entries in Table 24 in that it is substantially more labile to aquation than the simple inorganic systems but is significantly less reactive than keto and aldehyde complexes of chromium(III).[31,142,161,162] In this respect, complex V-1 resembles the terephthalonitrile complex of $(H_2O)_5Cr^{3+}$.[95] It should be noted that these two nitrile-bonded systems may not be typical nitriles because the

Table 24

Rate Constants for Aquation of Some $(H_2O)_5Cr^{III}X$ Complexes.[a]

X	k_1,[b] s^{-1}	k_2K_a,[c] $M\ s^{-1}$	Reference
NC_5H_5	1.2×10^{-8}	1.0×10^{-10}	160
Cl^-	2.8×10^{-7}	2.8×10^{-8}	84
Br^-	3.8×10^{-6}	9.0×10^{-7}	157
I^-	8.4×10^{-5}	3.4×10^{-5}	84
SCN^-	1.7×10^{-5}	2.7×10^{-6}	159
ONO_2^-	7.2×10^{-5}	1.4×10^{-7}	158
NCCH=CHCN	1.2×10^{-2}	4.1×10^{-4}	This work
$HC(O)C_6H_4CO_2H$	24.4	-	31
$HC(O)C_6H_4CH{=}CHCO_2H$	7.6	-	161
$CH_3C(O)C_6H_4C{\equiv}N$	-	0.91	162

[a] Values reported are at 25°C.

[b] Values for acid independent pathway.

[c] Values for inverse acid dependent pathway.

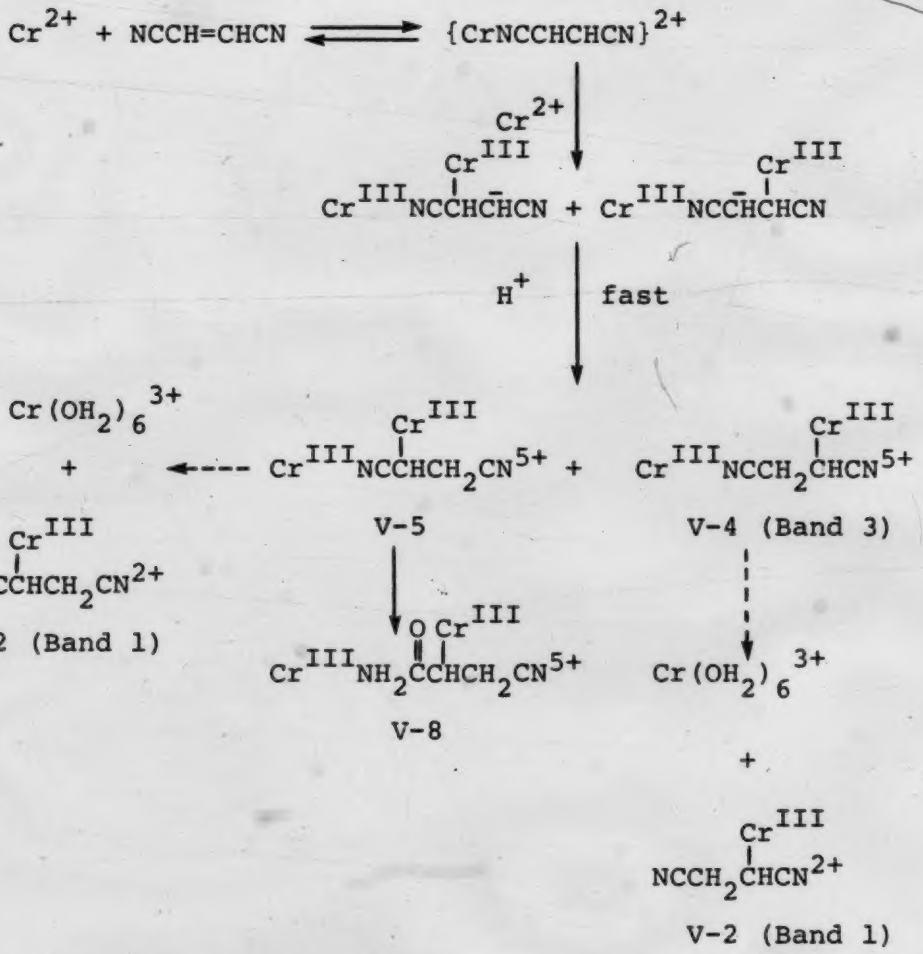
electron-withdrawing groups N≡CCH=CH- and $N{\equiv}CC_6H_4$- would be expected to weaken the chromium to nitrogen bond. Indeed, there is some evidence that the acetonitrile complex $(H_2O)_5CrN{\equiv}CCH_3{}^{3+}$, formed by oxidation of aqueous solutions of acetonitrile containing chromium(II), undergoes aquation less rapidly.[163]

The reactions of chromium(II) with free fumaronitrile and the chromium(III)-fumaronitrile complex V-1 differ from one another in that the latter is reduced about 1000 times faster. In both reactions, the dominant pathway is second order in chromium(II), but the mixture of products seems quite unrelated at first sight. However, the predominant products can be rationalized on the basis of a common reaction scheme which involves an initial equilibrium to form a chromium-fumaronitrile complex followed by rate controlling reduction by a second chromium(II) and proton addition. An additional principle involved in formulating the reaction schemes is the assumption that a nitrile bound to a chromium(III) with another chromium(III) on the α-carbon is rapidly hydrolyzed to a carboxamide. Such a nitrile group might be expected to be particularly susceptible to hydrolysis because of the high charge of the complex and the proximity of the two electron-withdrawing $(H_2O)_5Cr^{3+}$ moieties.

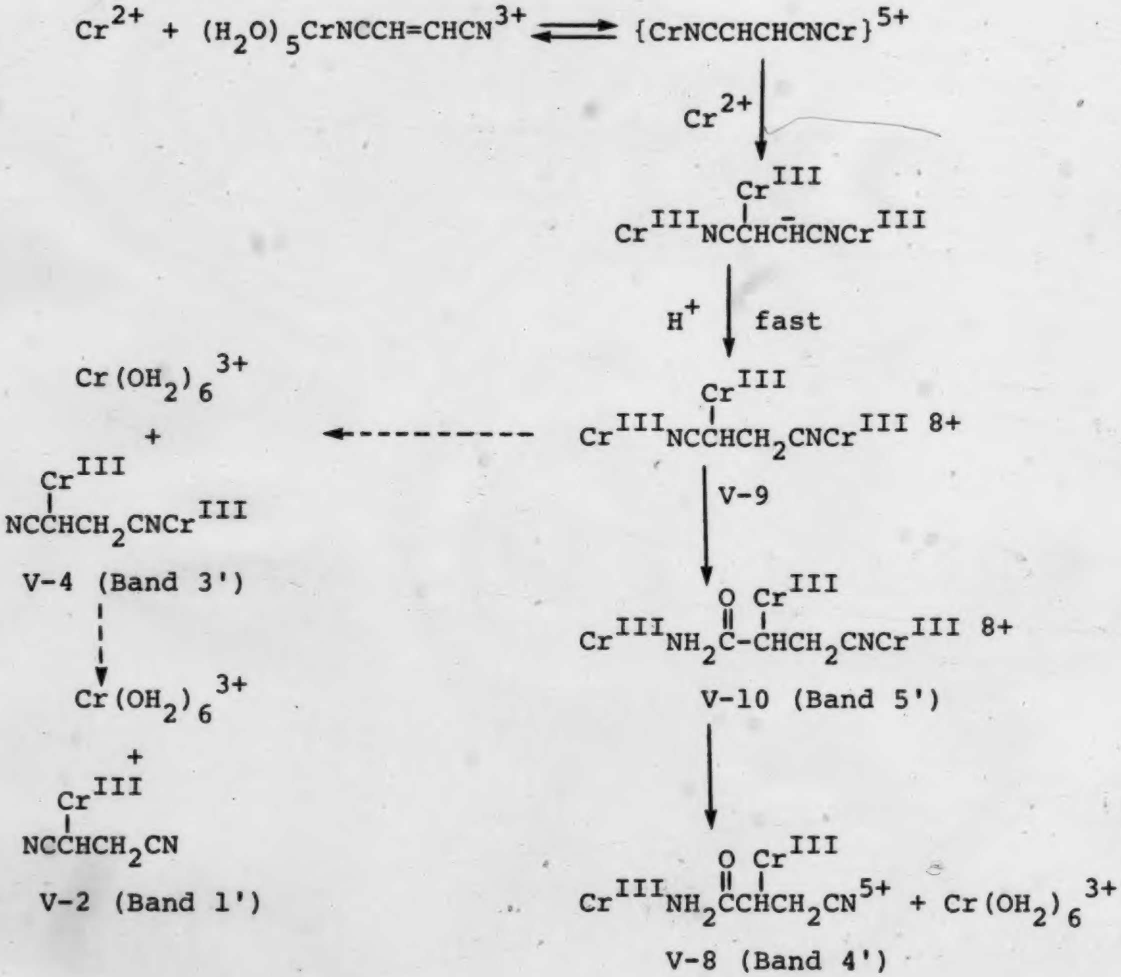
The reaction schemes are formulated initially in a minimal way without specifying the electron distribution in the initial complex. For free fumaronitrile, the proposed reaction scheme is shown in Scheme (5.24). Attack of chromium(II) on the initially formed $\{CrNCCHCHCN\}^{2+}$ complex and subsequent protonation yields a mixture of complexes V-4 and V-5. Complex V-4 might be the predominant product on steric grounds. In any event, V-5 could undergo decomposition to yield V-8 since, as noted earlier, the nitrile group coordinated to chromium(III) and adjacent to the organochromium(III) entity might be activated toward hydrolysis. However, complex V-8 was not observed, possibly because complex V-5, from which it would be formed, is only produced in a small yield. It is also possible that any V-8 that was produced could have been eluted with later fractions of Band 3 since its elution properties (as observed for complex V-8 formed in the reduction of V-1) are similar to that of V-4. Nevertheless Scheme (5.24) is consistent with the isolation of V-4 as the predominant species (~68%).

The analogous scheme for the reduction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$, V-1, is shown in Scheme (5.25). In this case, the intermediate $\{CrNCCHCHCNCr\}^{5+}$ is assumed to be symmetrical (a chromium on each nitrile) and reduction by a second chromium(II) and protonation produces only one initial product, V-9, which is rapidly hydrolyzed to complex V-10. Indeed, absorbance changes observed at 355 nm and 750 nm may correspond to such a reaction

Scheme (5.24)

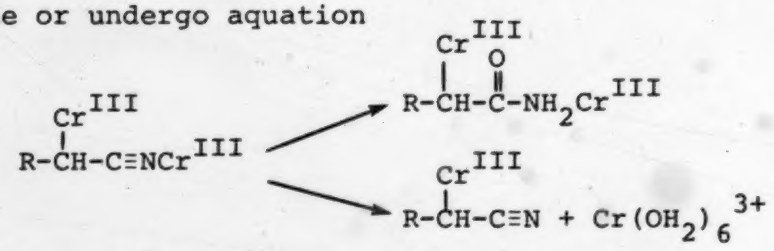

Cr2+ + NCCH=CHCN ⇌ {CrNCCHCHCN}2+
Cr2+
CrIII
CrIIINCCHCHCN + CrIIINCCHCHCN
H+
fast
Cr(OH2)6 3+
+
CrIII
NCCHCH2CN2+
V-2 (Band 1)
CrIIINCCHCH2CN5+ +
V-5
CrIIINCCH2CHCN5+
V-4 (Band 3)
O CrIII
CrIIINH2CCHCH2CN5+
V-8
Cr(OH2)6 3+
+
NCCH2CHCN2+
V-2 (Band 1)

Scheme (5.25)


Cr2+ + (H2O)5CrNCCH=CHCN3+
{CrNCCHCHCNCr}5+
Cr2+
CrIII
CrIIINCCHCHCNCrIII
H+
fast
CrIII
CrIIINCCHCH2CNCrIII 8+
V-9
O CrIII
CrIIINH2C-CHCH2CNCrIII 8+
V-10 (Band 5')
O CrIII
CrIIINH2CCHCH2CN5+ + Cr(OH2)6 3+
V-8 (Band 4')
Cr(OH2)6 3+
+
CrIII
NCCHCH2CNCrIII
V-4 (Band 3')
Cr(OH2)6 3+
+
CrIII
NCCHCH2CN
V-2 (Band 1')

(k = 0.103 s^{-1}, 25°C, 0.50 M $LiClO_4$-$HClO_4$). However, aquation during the ion-exchange separation gives some V-8(Band 4') from V-10 (Band 5'). At high acid concentrations, Bands 4' and 5' contain about 11 and 69%, respectively, of the ligand to give a total of 80% of the ligand accounted for by this scheme. This scheme also predicts that the amount of $Cr(OH_2)_6^{3+}$ should be equal to or greater than the amount of Band 4', and this is consistent with the observations (Table 22).

If it is assumed, in addition, that species with adjacent chromiums can react competitively to give carboxamide or undergo aquation

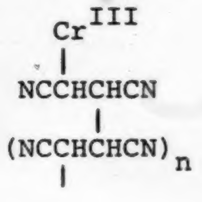


$$\text{R-}\overset{\text{Cr}^{\text{III}}}{\text{C}}\text{H-C}\equiv\text{NCr}^{\text{III}} \begin{cases} \longrightarrow \text{R-}\overset{\text{Cr}^{\text{III}}}{\text{C}}\text{H-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-NH}_2\text{Cr}^{\text{III}} \\ \longrightarrow \text{R-}\overset{\text{Cr}^{\text{III}}}{\text{C}}\text{H-C}\equiv\text{N} + \text{Cr(OH}_2)_6^{3+} \end{cases} \tag{5.26}$$

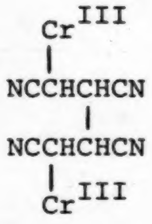
then further products can be accounted for. This is shown by the dotted arrows on the above schemes. Therefore, Scheme (5.24) shows that complex V-2 may be formed in the reduction of free fumaronitrile by aquation of complexes V-4 and V-5. Indeed, independent studies on V-4 revealed that it did undergo such a reaction (k = 3.60 x 10^{-4} s^{-1}, 25°C, 0.50 M $LiClO_4$-$HClO_4$). In any event, complex V-5 might be expected to undergo aquation more rapidly than V-4, and if the aquation should exhibit an inverse acid dependence typical of most chromium(III) complexes,[84,157-160] then this could account for the larger yields of V-2 observed at low acid concentrations (Table 19) where 75.4% of the fumaronitrile consumed is found as either V-2 or V-4. Similarly, as shown in Scheme (5.25), reduction of V-1 produces some V-4 by aquation of V-9, and the results in Table 22 reveal that more V-4 is obtained at low acid concentrations as expected from these assumptions. In addition, the small amounts of complex V-2 observed probably arise from aquation of V-4. In any event, Scheme (5.25) would account for 10.8% and 11.9% $Cr(OH_2)_6^{3+}$ at 0.388 M and 0.050 M $HClO_4$, respectively, compared to the observed values of 11.0% and 12.7%. Therefore, the products V-2, V-4, V-8, V-10 and $Cr(OH_2)_6^{3+}$ are accounted for with the $(H_2O)_5CrNCCH{=}CHCN^{3+}$ complex.

However, neither scheme accounts for the formation of the highly-charged species that were not easily eluted from the ion-exchange columns. These constitute Bands 4 (8.1-10.1%) and 5 (1.1-2.7%) in the reduction of free fumaronitrile and Band 6' (ca. 10%) in the reaction of V-1 with chromium(II). Similar highly charged complexes were observed in the chromium(II) reduction of maleic and fumaric acids,[37] although no attempt was made to establish their nature. Unfortunately, assigning the structure of these complexes is difficult since there is little additional information which would assist in their formulation. Nevertheless, it is interesting to speculate on their structure and how they are formed.

Although the yields of these species are small, it seems unlikely that they are chromium(III)-containing polymerization or radical coupling products of fumaronitrile such as



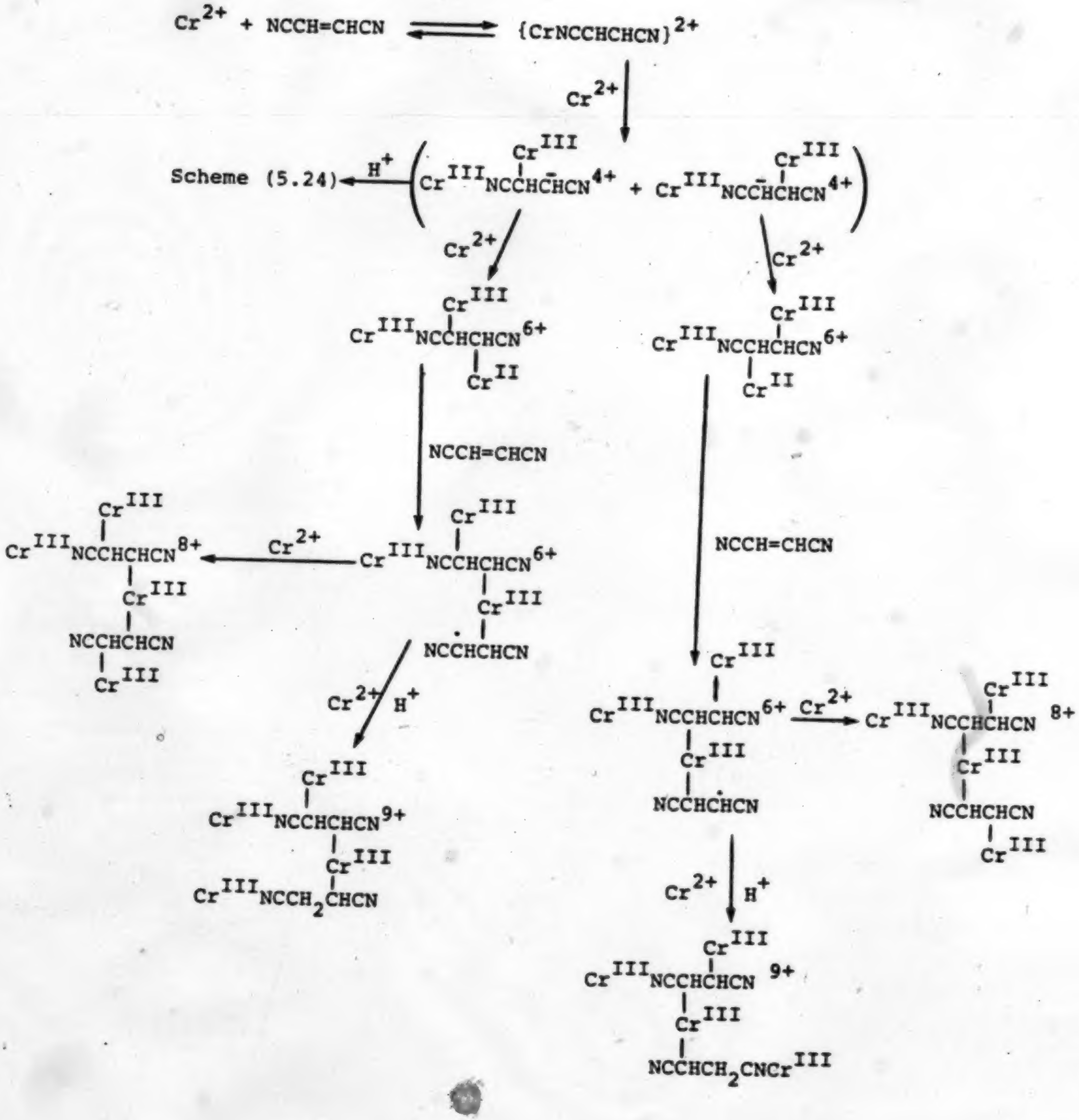
$$\begin{array}{c} Cr^{III} \\ | \\ NCCHCHCN \\ | \\ (NCCHCHCN)_n \\ | \end{array}$$



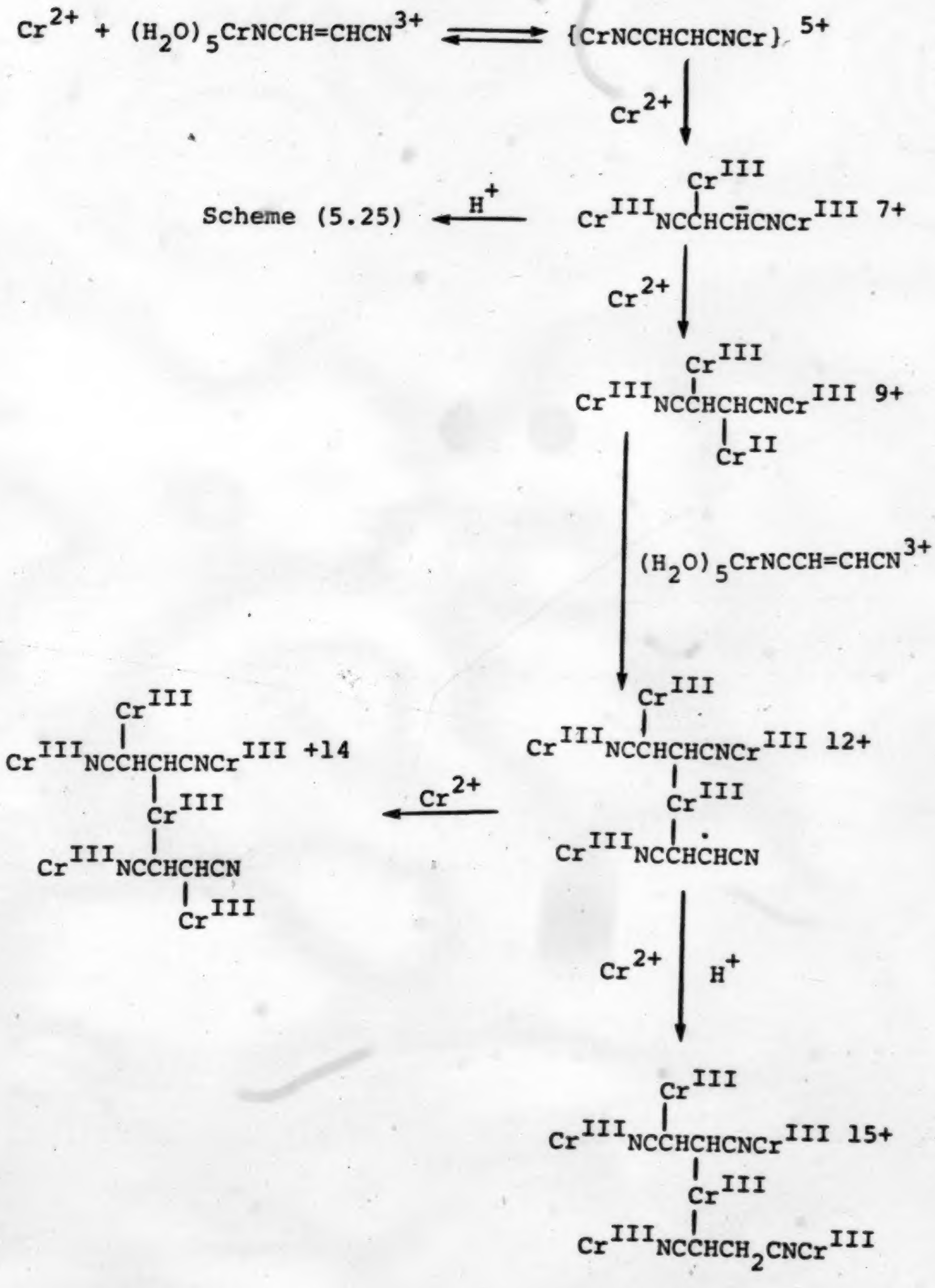
$$\begin{array}{c} Cr^{III} \\ | \\ NCCHCHCN \\ | \\ NCCHCHCN \\ | \\ Cr^{III} \end{array}$$

since lower stoichiometries than what were observed might have been expected. Rather, it is possible that the carbanionic complexes initially generated in Schemes (5.24) and (5.25) might react with additional chromium(II), as shown in Schemes (5.27) and (5.28). Both schemes require that complexation of chromium(II) to the carbanionic complexes be competitive with their protonation. Certainly, the water exchange rate of chromium(II) is very rapid $(k \simeq 2.9 \times 10^8\ s^{-1})$[164] and its binding to the nucleophilic carbon-centred anion might be expected to be very rapid also. In addition, these complexes might protonate at rates significantly less than diffusion controlled. Indeed, although less marked than nitro and ester derivatives, nitrile groups have been shown to appreciably decrease the rate of protonation of carbanions.[165-168] Presumably, this arises from some structural and electronic rearrangement within the anion which delocalizes the negative

Scheme (5.27)

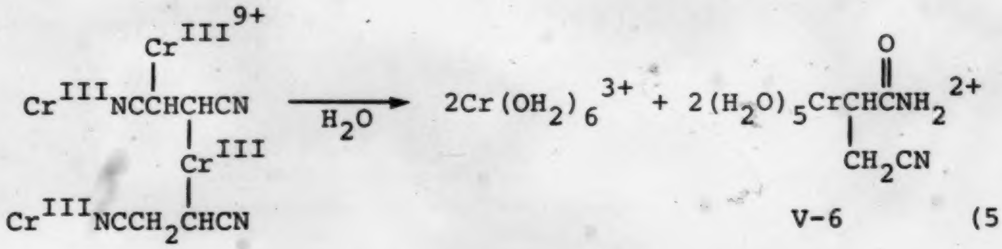

Cr2+ + NCCH=CHCN
{CrNCCHCHCN}2+
Cr2+
Scheme (5.24)
H+
CrIII
CrIIINCCHCHCN4+
+
CrIII
CrIIINCCHCHCN4+
Cr2+
Cr2+
CrIII
CrIIINCCHCHCN6+
CrII
CrIII
CrIIINCCHCHCN6+
CrII
NCCH=CHCN
NCCH=CHCN
CrIII
CrIIINCCHCHCN8+
CrIII
NCCHCHCN
CrIII
Cr2+
CrIII
CrIIINCCHCHCN6+
CrIII
NCCHCHCN
Cr2+
H+
CrIII
CrIIINCCHCHCN9+
CrIII
CrIIINCCH2CHCN
CrIII
CrIIINCCHCHCN6+
CrIII
NCCHCHCN
Cr2+
CrIII
CrIIINCCHCHCN 8+
CrIII
NCCHCHCN
CrIII
Cr2+
H+
CrIII
CrIIINCCHCHCN 9+
CrIII
NCCHCH2CNCrIII

Scheme (5.28)


Cr2+ + (H2O)5CrNCCH=CHCN3+
{CrNCCHCHCNCr} 5+
Cr2+
Scheme (5.25)
H+
CrIII
CrIIINCCHCHCNCrIII 7+
Cr2+
CrIII
CrIIINCCHCHCNCrIII 9+
CrII
(H2O)5CrNCCH=CHCN3+
CrIII
CrIIINCCHCHCNCrIII +14
CrIII
CrIIINCCHCHCN
CrIII
Cr2+
CrIII
CrIIINCCHCHCNCrIII 12+
CrIII
CrIIINCCHCHCN
Cr2+
H+
CrIII
CrIIINCCHCHCNCrIII 15+
CrIII
CrIIINCCHCH2CNCrIII

charge. In the present series of carbanionic complexes, the additional presence of chromium(III) moieties on the ligand might be expected to further decrease the rate of protonation. In any event, the alkyl-bound chromium(II) complexes could then react with either free fumaronitrile (Scheme (5.27)) or complex V-1 (Scheme (5.28)) and subsequently be reduced by an additional equivalent of chromium(II). This step may proceed by attack at either the radical carbon or at the adjacent nitrile followed by protonation. On the basis of results already described for the reaction of $NCCH_2\cdot$ with chromium(II) (Chapter IV), attack at the nitrile might be preferred.

The net charge of these complexes may be sufficiently large as to make elution of these species on the ion-exchange resin very difficult, as was observed. In addition, it would not be surprising if these products would undergo decomposition.



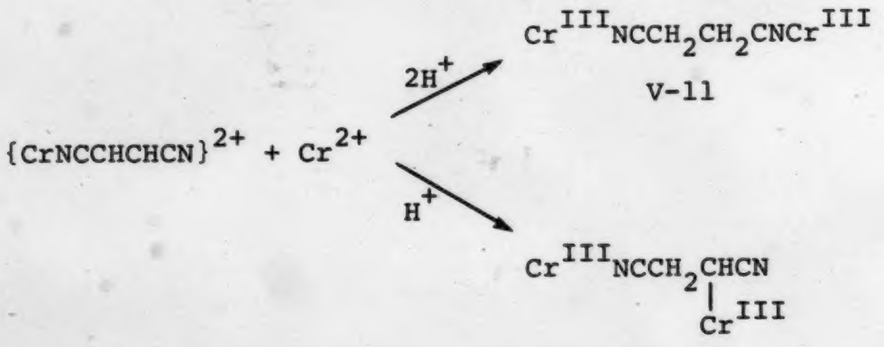
$$\begin{array}{l} \qquad\quad Cr^{III^{9+}} \\ \qquad\quad | \\ Cr^{III}NCCHCHCN \\ \qquad\qquad\;\; | \\ \qquad\qquad\;\; Cr^{III} \\ \qquad\qquad\;\; | \\ Cr^{III}NCCH_2CHCN \end{array} \xrightarrow[H_2O]{} 2Cr(OH_2)_6^{3+} + 2(H_2O)_5Cr\underset{\underset{CH_2CN}{|}}{CH}\overset{\overset{O}{\|}}{C}NH_2^{2+}$$

V-6 (5.29)

Equation (5.29) suggests that chromium(III)-bound nitrile groups may undergo hydrolysis to yield carboxamide complexes which may then aquate to yield $Cr(OH_2)_6^{3+}$ and organo-chromium(III) products. Such a decomposition process was observed for Band 4 which was obtained in the free fumaronitrile system. In fact, the reaction produced equivalent amounts of $Cr(OH_2)_6^{3+}$ and an organochromium(III) species whose electronic spectrum was identical with that of V-6 obtained from aquation of V-10. Similar decomposition may also be occuring for the products of Scheme (5.28). In this case, however, owing to the much higher charge of this complex, decomposition may not have proceeded to a sufficient extent during the same time interval (2 days) to yield complexes of low enough charge to be eluted from the resin.

The observation that only slightly smaller yields of the highly-charged complexes are formed at low acid concentrations could be taken as evidence against Schemes (5.27) and (5.28). However, protonation of the carbanionic complexes could be brought about by interaction with water,[169] rather than acid, in which case the yields of these complexes would be expected to be invariant with changing $[H^+]$. Schemes (5.27) and (5.28) would also predict that larger amounts of these highly-charged complexes should be formed at higher chromium(II) concentrations. However, this was not examined. In any event, Schemes (5.27) and (5.28) are speculative in nature and await futher confirmation.

The major product difference between the reduction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$, V-1, and free fumaronitrile is the larger amount of $Cr(OH_2)_6^{3+}$ produced with the latter. In fact, virtually all of the $Cr(OH_2)_6^{3+}$ found from reduction of V-1 can be accounted for by the aquation of organochromium(III) complexes, as shown in Scheme (5.25) and described earlier. On the other hand, even after correcting for the aquation of V-4 and V-5, up to 21% of the chromium(III) formed in the reduction of free fumaronitrile is found as $Cr(OH_2)_6^{3+}$ (Table 20). In addition, unlike the reduction of V-1 in which essentially all of the reduced fumaronitrile is found coordinated to chromium(III), less than 85% of the ligand is recovered as chromium(III) products in the reduction of free fumaronitrile. Both observations are unaccounted for by Schemes (5.24) and (5.27). It may be that the large yield of $Cr(OH_2)_6^{3+}$ arises from outer-sphere reduction of free fumaronitrile. Alternatively, it may result from competitive reactions of chromium(II) at either the carbon or nitrile nitrogen of the chromium-fumaronitrile precursor complex as shown in reaction (5.30).



$$\{CrNCCHCHCN\}^{2+} + Cr^{2+} \begin{array}{l} \xrightarrow{2H^+} Cr^{III}NCCH_2CH_2CNCr^{III} \quad \text{V-11} \\ \xrightarrow{H^+} Cr^{III}NCCH_2\underset{\overset{|}{Cr^{III}}}{CH}CN \quad \text{V-4} \end{array} \qquad (5.30)$$

Species V-11 would aquate to $Cr(OH_2)_6^{3+}$ and succinonitrile. That these paths are competitive is consistent with the observations in the Cr^{2+}-$NCCH_2I$ system (Chapter IV), where only 25% organochromium(III) product is formed.

Such a reaction scheme also explains why no $Cr(OH_2)_6^{3+}$ is formed directly in the reduction of V-1. In this case, both nitrile groups in the precursor complex $\{CrNCCHCHCNCr\}^{5+}$ are complexed to chromium, and attack of chromium(II) can only occur at carbon. Therefore, only organochromium(III) products would be formed which is consistent with the product analysis results.

To this point in the discussion, the precursor complexes have been formulated in a general manner without specifying the electron distribution. Two different formulations are possible. The precursor complexes might arise simply from reductant binding at available nitrile groups as shown in equations (5.31) and (5.32).

$$Cr^{2+} + NCCH{=}CHCN \overset{K_1}{\rightleftharpoons} Cr^{II}NCCH{=}CHCN \xrightarrow[Cr^{2+}]{k_2} \text{Products} \qquad (5.31)$$

$$Cr^{2+} + Cr^{III}NCCH{=}CHCN \overset{K_1}{\rightleftharpoons} Cr^{III}NCCH{=}CHCNCr^{II} \xrightarrow[Cr^{2+}]{k_2} \text{Products} \qquad (5.32)$$

Then reduction of the ligand does not proceed until attack of the second equivalent of chromium(II) so that the reaction rate has the observed second-order dependence on chromium(II). Alternatively the precursor complexes may be considered as radical anions formed in an unfavourable equilibrium from chromium(II) and the olefin as shown in equations (5.33) and (5.34).

$$\mathrm{Cr}^{2+} + \mathrm{NCCH{=}CHCN} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cr}^{III}\text{-}(\mathrm{NCCHCHCN})^{\dot{-}} \xrightarrow[\mathrm{Cr}^{2+}]{k_2} \text{Products} \qquad (5.33)$$

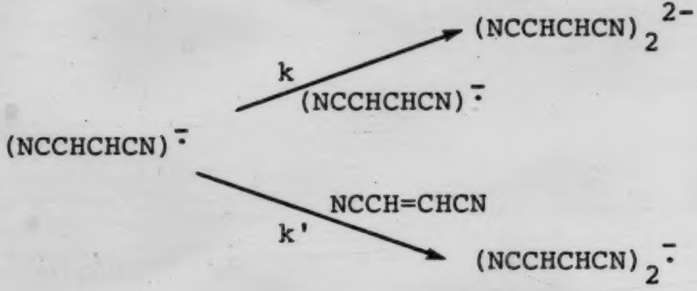
$$\begin{tikzcd} \mathrm{Cr}^{2+} + \mathrm{Cr}^{III}\mathrm{NCCH{=}CHCN} \arrow[r, shift left, "k_1"] & \mathrm{Cr}^{III}\text{-}(\mathrm{NCCHCHCN})^{\dot{-}}\text{-}\mathrm{Cr}^{III} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2"', "\mathrm{Cr}^{2+}"] \\ & \text{Products} \end{tikzcd} \qquad (5.34)$$

If a steady state is assumed for the radical anion, then the apparent rate constant is given by equation (5.35).

$$k_{obsd} = \frac{k_1 k_2 [\mathrm{Cr}^{2+}]^2}{k_{-1} + k_2 [\mathrm{Cr}^{2+}]} \qquad (5.35)$$

This will give a second-order dependence on chromium(II) if $k_{-1} \gg k_2[\mathrm{Cr}^{2+}]$. It is noteworthy that equation (5.35) predicts a first-order chromium(II) dependence if $k_{-1} \ll k_2[\mathrm{Cr}^{2+}]$. This is consistent with the observed rate law for reduction of maleic and fumaric acids by chromium(II).[147] Since reactions between chromium(II) and aliphatic radicals are known to be facile ($k_2 \simeq (0.35\text{-}3.5) \times 10^8\ M^{-1}\ s^{-1}$),[81] it seems likely that changes in k_{-1} will be most important in determining which limiting condition applies to equation (5.35). Therefore, it could be argued that nitrile groups are better electron mediators than carboxylate groups,[170,171] and as such, k_{-1} would be expected to be larger for fumaronitrile than for the carboxylates. This provides a rationalization for the different chromium(II) dependencies in the fumaronitrile system and carboxylate systems.

The failure to observe radical coupling seems to be an argument against the radical mechanism. However the reactions of the fumaronitrile radical anion with itself or unreduced fumaronitrile have been studied in dimethylformamide[172]


(NCCHCHCN)$_2^{2-}$
k
(NCCHCHCN)$^{\bar{\cdot}}$
(NCCHCHCN)$^{\bar{\cdot}}$
NCCH=CHCN
k'
(NCCHCHCN)$_2^{\bar{\cdot}}$

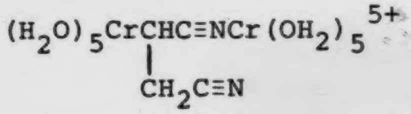
(5.36)

and estimates of 7 x 10^5 M^{-1} s^{-1} and 1 x 10^4 M^{-1} s^{-1} were obtained for k and k', respectively. Under the conditions of the present study where the concentration of fumaronitrile or any radical species would be much smaller than that of chromium(II), it is very unlikely that reactions analogous to those of scheme (5.36) would be competitive with attack by chromium(II).

Another argument that could be brought against the radical mechanism is that the chromium(III) radical anion intermediate should undergo rapid protonation and, as a result, exhibit a first-order dependence on $[H^+]$ which is not observed. However, as noted earlier, protonations of carbanions are not always diffusion controlled, and it is not certain that the proposed radical anion intermediates would protonate that rapidly. Alternatively, protonation could be from the solvent water, in which case a first-order acid dependence would not be expected, provided that the reverse reaction is slow and the equilibrium lies far to the right (protonated form).

The above discussion is intended to illustrate that the radical mechanism may not be as unlikely as it might appear initially. However, these arguments do not exclude the simple chromium(II) precursor complex formation scheme of equations (5.31) and (5.32). The latter could account for the different rate laws by supposing rate-controlling electron transfer within the precursor complex for the carboxylates, and rate-controlling reduction of the precursor complex for fumaronitrile by a second equivalent of chromium(II).

As noted earlier, a simple third-order rate law[173] is found for the reduction of free fumaronitrile if the reaction is monitored at 750 nm or by quenching, but an inverse acid dependence appears when monitoring the reaction at 520 nm. The simplest explanation for this behaviour is the formation of an intermediate which does not absorb in the 750 nm region but which does absorb at 520 nm, and thereby affects the spectroscopically determined rate law at this wavelength. The nature of this species is uncertain, but on the basis of results already discussed, it may correspond to complexes V-5 or V-11.



$(H_2O)_5Cr\underset{\substack{|\\ CH_2C\equiv N}}{C}HC\equiv NCr(OH_2)_5^{5+}$

V-5

$(H_2O)_5CrN\equiv CCH_2CH_2C\equiv NCr(OH_2)_5^{6+}$

V-11

Both species have been proposed as unstable products of the reduction reaction and both might be expected to exhibit an inverse acid dependence[84,157-160] during their aquation to stable products. This may account for the apparent acid dependence of the reduction reaction when monitored at 520 nm.

In light of the above discussion for the free fumaronitrile system, it is uncertain whether the complicated rate law (equation (5.22)) obtained for reduction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$, V-1, truly represents the mechanism of reduction of V-1 or whether, as for free fumaronitrile at 520 nm, it arises as a result of the formation of an absorbing intermediate. Unfortunately, quenching experiments analogous to those employed in the free fumaronitrile system were impossible owing to the rapid rate of the reduction. In addition, preliminary studies at

750 nm did not give the anticipated absorbance decrease expected for loss of chromium(II). Presumably, the absorbance increase attributed to the organochromium(III) products formed is greater than the small absorbance decrease for oxidation of chromium(II) at this wavelength. Nevertheless, this result, coupled with the apparent wavelength dependence of k_{obsd}^{corr}, leads to some uncertainty in the reliability of the kinetic data to formulate the mechanism of reduction of V-1. Clearly, both possibilities must be considered.

If the kinetic results actually reflect the mechanism of reduction of V-1, then the following scheme is consistent with these results:

$$\begin{tikzcd}
 & & \text{"X"} \arrow[d, shift left] \\
(H_2O)_5CrNCCH{=}CHCN^{3+} + Cr^{2+} \arrow[d, shift right, "K_a"'] \arrow[rr, shift left, "K_1"] & & \{(H_2O)_5CrNCCHCHCNCr(OH_2)_5\}^{5+} \arrow[ll, shift left] \arrow[u, shift left, "K_2"', "+\,H^+"] \arrow[d, "k_2"', "Cr^{2+}"] \\
(H_2O)_4(HO)CrNCCH{=}CHCN^{2+} + H^+ \arrow[u, shift right] \arrow[d, "k_1"', "Cr^{2+}"] & & \text{Products} \\
\text{Products} & &
\end{tikzcd}$$

(5.37)

Species "X" is a complex whose nature will be discussed later. In addition, the precursor complex has been formulated in only a minimal manner and can represent the assignments of either equation (5.32) or (5.34).

The derived first-order rate constant (k_{obsd}^{corr}) takes the form

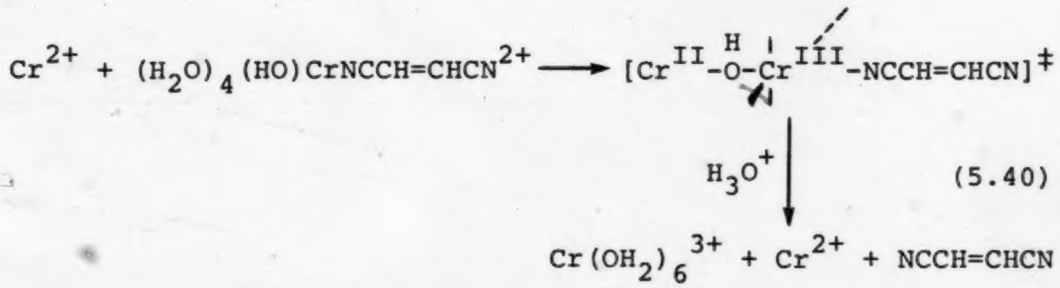
$$k_{obsd}^{corr} = \frac{(k_1K_a + k_2K_1[H^+][Cr^{2+}])[Cr^{2+}]}{[H^+]+K_a+K_1[H^+][Cr^{2+}](1+K_2[H^+])} \qquad (5.38)$$

If $K_2[H^+] >> 1$, and if $K_a << [H^+] + K_1K_2[H^+]^2[Cr^{2+}]$, then

$$k_{obsd}^{corr} = \frac{(\frac{k_1K_a}{[H^+]} + k_2K_1[Cr^{2+}])[Cr^{2+}]}{1 + K_1K_2[H^+][Cr^{2+}]} \qquad (5.39)$$

which is of the same form as that obtained experimentally (equation (5.22)). The various terms have the following values: $k_1K_a = (1.7 \pm 0.5) \times 10^{-1}\ s^{-1}$, $k_2K_1 = (2.01 \pm 0.12) \times 10^3\ M^{-2}\ s^{-1}$, and $K_1K_2 = (5.5 \pm 1.5) \times 10^1\ M^{-2}$ (25°C, 0.50 M $LiClO_4$-$HClO_4$).

The products of the k_2 reaction are assumed to be the organochromium(III) complexes already formulated in Schemes (5.25) and (5.28). On the other hand, the k_1 pathway may not yield organochromium(III) products since it is unclear why deprotonation of a water molecule on complex V-1 should facilitate organochromium(III) product formation. However, the k_1 pathway can be accounted for if, rather than ligand reduction, the reaction pertains to chromium(II) catalyzed aquation, according to the reaction



$$\mathrm{Cr^{2+} + (H_2O)_4(HO)CrNCCH{=}CHCN^{2+}} \longrightarrow \mathrm{[Cr^{II}\text{-}\overset{H}{O}\text{-}Cr^{III}\text{-}NCCH{=}CHCN]^{\ddagger}} \xrightarrow{\mathrm{H_3O^+}} \mathrm{Cr(OH_2)_6^{3+} + Cr^{2+} + NCCH{=}CHCN} \qquad (5.40)$$

where inner-sphere electron transfer through a bridging OH group occurs.

As evidence in support of the assignment, Figure 19 illustrates that there is a linear relationship between the uncatalyzed (k_{uncat}) and chromium(II) catalyzed (k_{cat}) inverse acid dependent aquation terms for halide complexes of $Cr(OH_2)_5^{3+}$.[84-86,157,174] In the chromium(II) catalyzed reactions, the inverse acid dependent path arises from inner-sphere reduction via a bridging OH group. Such a relationship between k_{cat} and k_{uncat} may not be accidental. Indeed, just as stretching of the Cr-X bond is an obvious requirement for release of X in the uncatalyzed aquations, distortions along the Cr-X bond may lower the energy of the acceptor orbital on chromium(III),[104,105] thereby facilitating its reduction by chromium(II). In any event, the observation that $(H_2O)_5CrNCCH{=}CHCN^{3+}$ follows the pattern established by the halide complexes may suggest that it does undergo chromium(II) catalyzed aquation by inner-sphere electron transfer, as suggested above.

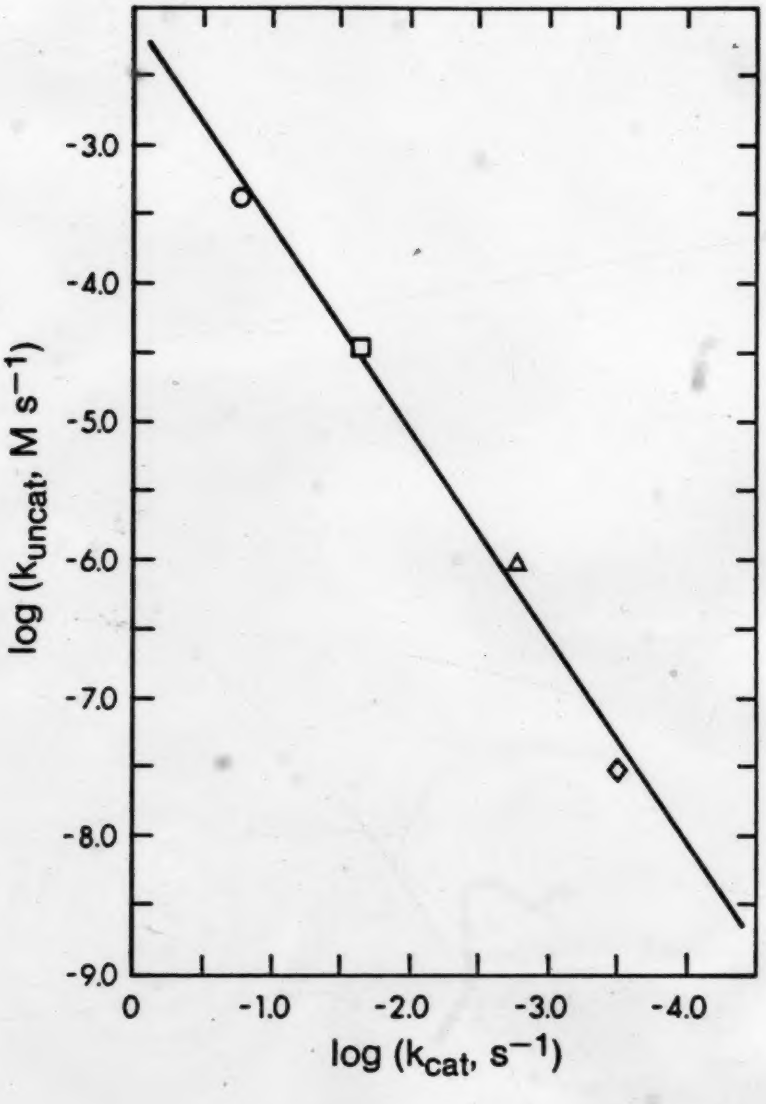
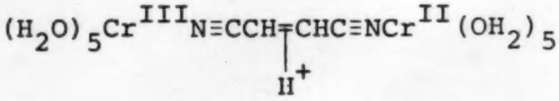


FIGURE 19. A plot of the uncatalyzed (log(k_{uncat})) versus chromium(II)-catalyzed (log(k_{cat})) inverse-acid dependent aquation terms for $(H_2O)_5CrX^{2+}$: (○) $-CH_2CN$; (□) -I; (△) -Br; (◇) -Cl.

Much more difficult to explain is the nature of "X" in scheme (5.37). The kinetic data require that it is formed by protonation of the precursor complex and is in rapid equilibrium with it. If the precursor complex is formulated as in equation (5.32), then "X" could be



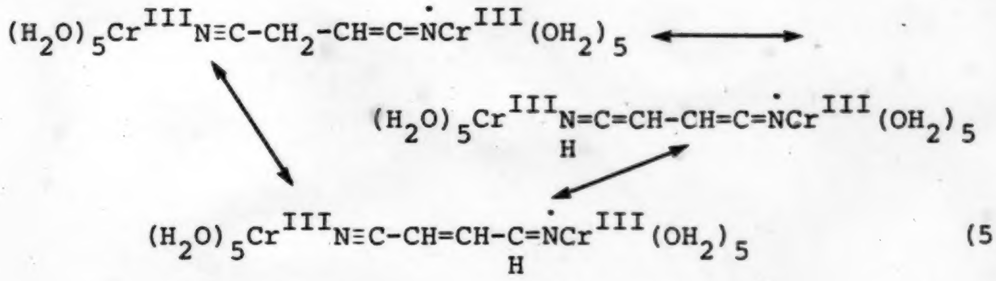
$$\mathrm{(H_2O)_5Cr^{III}N{\equiv}CCH\underset{H^+}{=}CHC{\equiv}NCr^{II}(OH_2)_5}$$

where a proton has become associated with the double bond, or perhaps with one of the nitrile groups. However, this is very unlikely since independent experiments on free fumaronitrile suggest no such interaction. Alternatively, if the precursor complex is formulated as a radical anion species, then its protonation could be represented by equation (5.41).

$$\mathrm{(H_2O)_5Cr^{III}NC\overset{-}{C}H\overset{\cdot}{C}HCNCr^{III}(OH_2)_5 + H^+ \rightleftharpoons}$$

$$\mathrm{(H_2O)_5Cr^{III}NCCH_2\overset{\cdot}{C}HCNCr^{III}(OH_2)_5} \qquad (5.41)$$

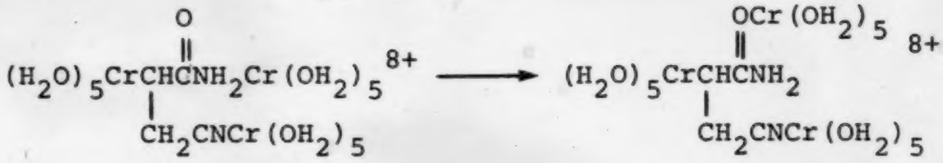
However, this protonated radical would be expected to be rapidly reduced by chromium(II), a feature that is inconsistent with the proposed mechanism. It could be argued that the protonated radical may exist in other resonance forms such as



$$(H_2O)_5Cr^{III}N\equiv C-CH_2-CH=C=\dot{N}Cr^{III}(OH_2)_5 \longleftrightarrow (H_2O)_5Cr^{III}\underset{H}{N}=C=CH-CH=C=\dot{N}Cr^{III}(OH_2)_5 \longleftrightarrow (H_2O)_5Cr^{III}N\equiv C-CH=CH-\underset{H}{C}=\dot{N}Cr^{III}(OH_2)_5 \qquad (5.42)$$

where additional reduction by chromium(II) may be inhibited because of steric restraints around the chromium(III)-bound nitrogen-centred radical. Indeed, evidence for nitrogen-centred radicals has been obtained for reaction of hydrogen atoms and solvated electrons with aliphatic nitriles[175,176] and also in the reactions of $e^-_{(aq)}$ with acrylonitrile.[177] However, the required lack of reactivity of "X" toward chromium(II) is still troublesome, even if "X" is of the type shown in equation (5.42), since outer-sphere reduction of the radical might have been expected to be sufficiently facile to yield reduced products. Indeed, our inability to devise a reasonable formulation of "X" may imply that scheme (5.37) is not operative. This, in turn, may suggest that the kinetic data from which the scheme was proposed may be affected by some other reaction or absorbing intermediate. This is consistent with the observed wavelength dependence of k^{corr}_{obsd}.

The nature of such an intermediate is uncertain. It may possibly have a structure analogous to complexes V-5 or V-11 which were proposed to account for the apparent acid dependence observed for the reduction of free fumaronitrile at 520 nm. Alternatively, it may arise from the rapid decomposition of the initially formed complex V-9 to other organochromium(III) products. Indeed, such a reaction was observed at 355 and 750 nm (k = 0.103 $M^{-1}\ s^{-1}$) and was tentatively ascribed to the hydrolysis of the α-nitrile in V-9 to yield the nitrogen-bound carboxamide complex V-10. However, as noted earlier, it is possible that V-10 is the oxygen-bonded isomer. On this basis, it is possible that the reaction observed at 355 and 750 nm is the isomerization reaction



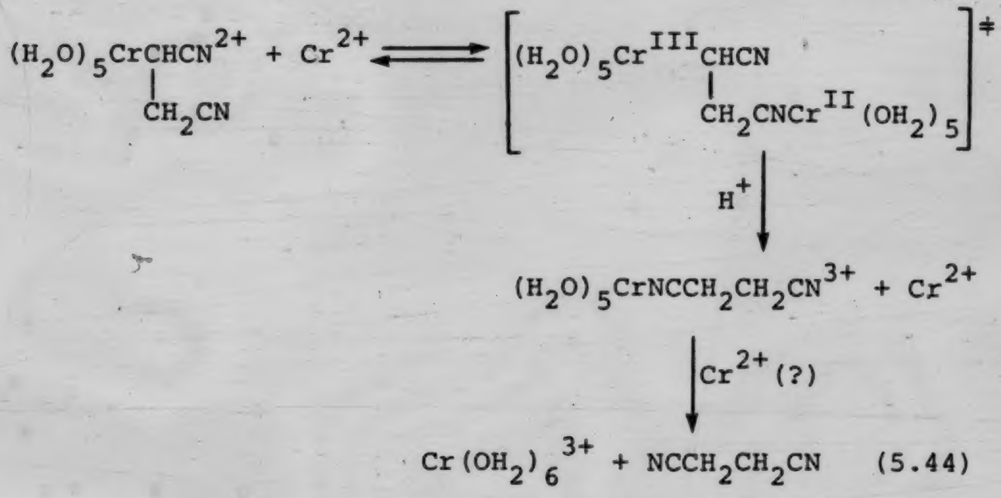
$$(H_2O)_5Cr\underset{\underset{CH_2CNCr(OH_2)_5}{|}}{CH}\overset{\overset{O}{\|}}{C}NH_2Cr(OH_2)_5^{8+} \longrightarrow (H_2O)_5Cr\underset{\underset{CH_2CNCr(OH_2)_5}{|}}{CH}\overset{\overset{OCr(OH_2)_5}{\|}}{C}NH_2^{\;8+} \qquad (5.43)$$

If this is assumed, then it obviously necessitates that the hydrolysis of V-9 precedes this reaction and it may be that the reaction is competitive with the formation of V-9. Since it might not be surprising that hydrolysis of the α-nitrile would be inversely dependent on $[H^+]$, this may also account for the apparent acid dependence of k_{obsd}^{corr}. In any event, this is one way to account for the results.

In comparing the chromium(II) reductions of free fumaronitrile and complex V-1, it is clear that the attachment of the chromium(III) moiety in V-1 has increased the rate of reduction of the ligand by about 10^3 times. This is expected since coordination of $(H_2O)_5Cr^{3+}$ would enhance the electron acceptor properties of the ligand, thereby making it more reducible. A similar rate enhancement might be expected for the analogous maleate and fumarate complexes of chromium(III). However, based on the results of other workers, this does not seem to be the case. Although the kinetics have not been studied in detail, it appears that the monodentate and chelated chromium(III) complexes of maleic acid undergo reduction of the coordinated ligand by at least a factor of ten less rapidly than for the free acid.[141,147] Results on the fumarate complex likewise suggest that the coordinated ligand is not readily reduced.[48,139,152] This difference in reactivity may result from the fact that in the free carboxylic acids, reduction of the fully protonated ligand occurs whereas in the chromium(III) analogues, the coordinated ligand has lost at least one proton. It has been shown that deprotonated maleic and fumaric acids are less reducible than the fully protonated acids.[178,179] Therefore, the decreased reactivity of the carboxylate complexes could be accounted for if the chromium(III) moiety is not as efficient as the proton in enhancing the reducibility of the ligands. Clearly, this is not a complicating feature in the fumaronitrile system.

Although the nature of the various organochromium(III) complexes formed in the reduction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$ and free fumaronitrile have been discussed at length, additional comment is required on the reactivity of some of these toward various reagents. For example, $(H_2O)_5CrCH(CN)CH_2CN^{2+}$, V-2, formed in the reduction of free fumaronitrile, is extremely stable to protolysis. In addition, it is unreactive to external oxidants such as O_2, Fe^{3+}, $(NH_3)_5CoN_3^{2+}$ and Ag^+. This suggests that the complex is not reactive to homolytic cleavage of the chromium-carbon bond.[35,180] Unlike many other organochromium(III) complexes,[79,87] V-2 reacts very slowly with mercury(II) ($k \simeq 3.2 \times 10^{-4}\ M^{-1}\ s^{-1}$). For comparison, $(H_2O)_5CrCH_2CN^{2+}$ is ca. 3×10^4 times more reactive.[87] Apparently, replacement of -H with the bulkier and more electron-withdrawing $-CH_2CN$ group has reduced dramatically the reactivity of complex V-2 for the mercury(II) electrophile.

Complex V-2 is readily reduced by chromium(II), resembling the reactivity of $(H_2O)_5CrCH_2CN^{2+}$ already described in Chapter IV. In this case, however, only an acid-independent pathway is observed ($k = 1.19 \times 10^{-2}$ $M^{-1}\ s^{-1}$, 0.50 M $LiClO_4$-$HClO_4$). As for $(H_2O)_5CrCH_2CN^{2+}$, it is difficult to understand why either inner-sphere electron transfer through a bridging H_2O molecule or simple outer-sphere reduction should be so much more rapid in this system than what is observed in other similar systems.[100-103] Rather, it is suggested that the reaction proceeds via a bridged-outer-sphere mechanism.



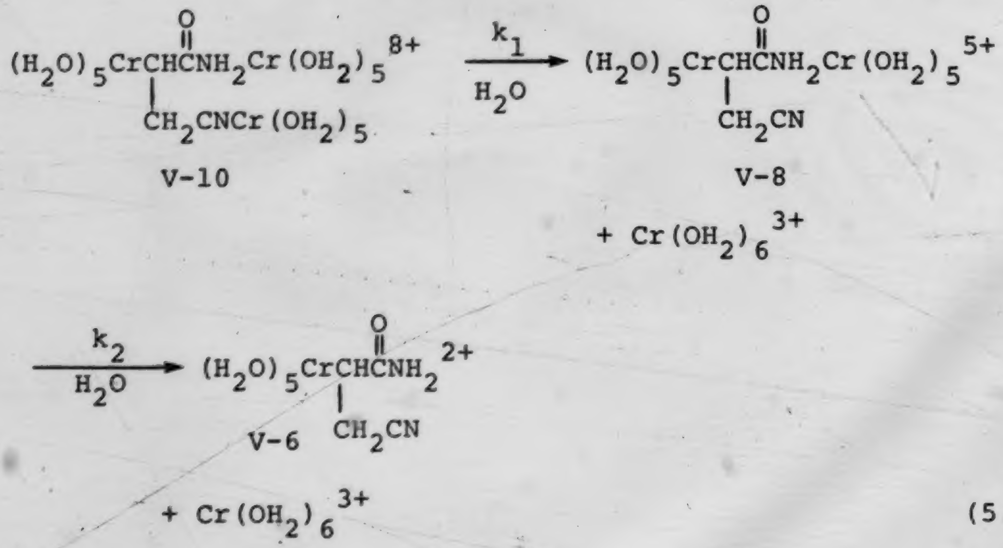
$$(H_2O)_5Cr\underset{\displaystyle CH_2CN}{\underset{|}{C}}HCN^{2+} + Cr^{2+} \rightleftharpoons \left[(H_2O)_5Cr^{III}\underset{\displaystyle CH_2CNCr^{II}(OH_2)_5}{\underset{|}{C}}HCN\right]^{\ddagger} \xrightarrow{H^+} (H_2O)_5CrNCCH_2CH_2CN^{3+} + Cr^{2+} \xrightarrow{Cr^{2+}(?)} Cr(OH_2)_6^{3+} + NCCH_2CH_2CN \quad (5.44)$$

The scheme suggests that chromium(II) binds at the β-nitrile, rather than at the α-nitrile group. This need not be the case, although there are some attractive reasons for suggesting this. Firstly, the β-nitrile might be expected to be the more basic of the two since it is somewhat insulated from the electron-withdrawing organochromium(III) entity by an additional methylene group. In addition, molecular models suggest that coordination at the β-nitrile provides closer approach of the two metal centres. This should facilitate direct electron transfer between the metals. Finally, if the earlier discussion (Chapter IV) of the reduction of $(H_2O)_5CrCH_2CN^{2+}$ is correct, then attack at the α-nitrile might be expected to yield a pathway that is inversely dependent on the acid concentration. However, this is not observed. In any event, whichever nitrile group is the site of reductant binding, the nitrile-bonded succinonitrile complex is generated. This complex can either aquate rapidly or undergo chromium(II) catalyzed aquation to yield the observed products.

The predominant product obtained in the reduction of free fumaronitrile with chromium(II) has been formulated as $(H_2O)_5CrCH(CN)CH_2CNCr(OH_2)_5{}^{5+}$, V-4, as compared to its linkage isomer V-5. This was assumed on steric grounds, although its related stability toward aquation corroborates this assignment. Certainly, complex V-4 undergoes facile aquation ($k = 3.6 \times 10^{-4}\ s^{-1}$) to $Cr(OH_2)_6{}^{3+}$ and complex V-2, yet it is ca. 30 times less reactive to aquation than are $(H_2O)_5CrNCCH{=}CHCN^{3+}$ and $(H_2O)_5CrNCC_6H_4CN^{3+}$.[95] If this dichromium(III) product was actually isomer V-5 with the second chromium(III) coordinated at the α-nitrile, then a rate of aquation closer to those observed for the fumaronitrile and terephthalonitrile complexes might be expected because of the lower basicity of this nitrile group. Indeed, it is interesting to note that the rates of aquation of V-4 and $(H_2O)_5CrNCCH_3{}^{3+}$ [163] are almost identical. In any event, the results suggest that not all nitrile-bonded chromium(III) complexes are as reactive to aquation as had been thought previously.[142]

It is not clear whether chromium(II) catalyzes the decomposition of complex V-4 since the kinetic data are insufficiently reliable to definitely show a chromium(II) dependent path. However, the results do indicate that any such catalysis is relatively unimportant at normal chromium(II) concentrations, when compared to the uncatalyzed aquation of V-4. Such behaviour is not unanticipated because the high charge of this complex would inhibit attack by chromium(II).

As noted earlier, the principal product initially formed in the reduction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$ is thought to be V-9 which then readily undergoes hydration of the α-nitrile to yield complex V-10. This facile hydrolysis probably results not only from the high charge of the complex but also by the proximity of two electron-withdrawing chromium(III) moieties near the α-nitrile. The assignment of complex V-10 as the nitrogen-coordinated carboxamide (or possibly the oxygen-bonded isomer) is further substantiated by the decomposition reactions observed (equation (5.45)).



$$\underset{\text{V-10}}{(H_2O)_5Cr\underset{CH_2CNCr(OH_2)_5}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}NH_2Cr(OH_2)_5^{8+}} \xrightarrow[H_2O]{k_1} \underset{\text{V-8}}{(H_2O)_5Cr\underset{CH_2CN}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}NH_2Cr(OH_2)_5^{5+}} + Cr(OH_2)_6^{3+}$$

$$\xrightarrow[H_2O]{k_2} \underset{\text{V-6}}{(H_2O)_5Cr\underset{CH_2CN}{\underset{|}{CH}}\overset{O}{\overset{\|}{C}}NH_2^{2+}} + Cr(OH_2)_6^{3+} \qquad (5.45)$$

Therefore, the value of k_1 (2.0×10^{-4} s^{-1}, 25°C, $[H^+]$ = 0.10 M, $[NaClO_4]$ = 0.1 M) is remarkably similar to the aquation rate constant for complex V-4 (3.6×10^{-4} s^{-1}, 25°C, 0.50 M $LiClO_4$-$HClO_4$), considering the different reaction conditions. This observation serves to corroborate the earlier suggestion that the nitrile-bound chromium(III) is aquated first. Indeed, the observation that there is a 10-fold decrease in the rate of aquations of V-8 ($k = 3.6 \times 10^{-5}$ s^{-1}, 25°C, $[H^+]$ = 0.10 M, $[NaClO_4]$ = 0.10 M) as compared to V-4 is further evidence in support of equation (5.45) since it is consistent with the expected greater Lewis basicity of the carboxamide in V-8 as compared to the nitrile in V-4. The value of k_2 for complex V-8 is also consistent with an oxygen-bonded carboxamide since the value is remarkably similar to the aquation rate constants observed for the oxygen-bonded complexes of nicotinamide and isonicotinamide.[24]

CHAPTER VI

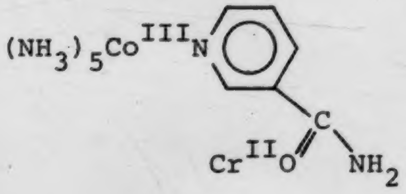
CONCLUSIONS

For a number of the complexes studied, complexation to $(NH_3)_5Co^{3+}$ has resulted in a change in the properties of the ligand. For example, coordination of cyanoacetic acid through the nitrile nitrogen has increased the acid dissociation constant of the ligand by a factor of ten.[181] Also, it was shown previously that complexation of malononitrile results in a decrease of the pK_a of the ligand from 11.3[182] to 5.7.[60] These changes can be attributed to the electron-withdrawing ability of the $(NH_3)_5Co^{3+}$ moiety. The electron-withdrawing influence of the metal centre has also been suggested as the reason that coordinated nitriles are more readily hydrolyzed to carboxamides than the free ligands.[183] Presumably, $(NH_3)_5Co^{3+}$ polarizes the nitrile bond making the carbon much more susceptible to nucleophilic attack by H_2O or hydroxide ion. Strongly electron-withdrawing groups on the ligand should accelerate hydrolysis also. Indeed, of the nitrile-coordinated cobalt(III) complexes studied here, it would appear that the malononitrile and fumaronitrile complexes are the most readily hydrolyzed in dilute acid. In addition, the large number of electron-withdrawing $(H_2O)_5Cr^{3+}$ moieties and nitrile groups in complex V-9, formed in the reduction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$, has been suggested as the reason for its facile hydrolysis to V-10.

A large part of the present work has centred around the involvement of a bridged-outer-sphere mechanism in reductions by chromium(II). In Chapter III, the reduction of several aliphatic nitrile complexes were studied. Based on rate arguments and product studies, the acetonitrile, succinonitrile, methylcyanoacetate and cyanoacetamide complexes of $(NH_3)_5Co^{3+}$ are believed to undergo reduction via a non-bridged-outer-sphere mechanism. On the other hand, the isolation of a ligand-transfer chromium(III) product in the reduction of the cyanoacetate complex suggests that reduction occurs within a bridged activated complex. Inner-sphere electron transfer is not possible because of the presence of a saturated methylene group in the ligand. Rather, a bridged-outer-sphere mechanism is suggested in which the ligand serves only to bring the two metal centres into close proximity to facilitate the electron transfer process.

The malononitrile complex may undergo reduction by a similar mechanism. This is based on the observation that the acid independent term ($k_1 = 0.0629\ M^{-1}\ s^{-1}$) is nearly three times larger than that for similar complexes which proceed by a non-bridged-outer-sphere mechanism. On the other hand, the inverse acid dependent term is most easily explained by a bridged-innner-sphere mechanism in which chromium(II) attacks the remote nitrile group of the deprotonated ligand. Unfortunately, the apparent lability of the chromium(III) malononitrile complex formed by both pathways precludes the unequivocal determination of the mechanism.

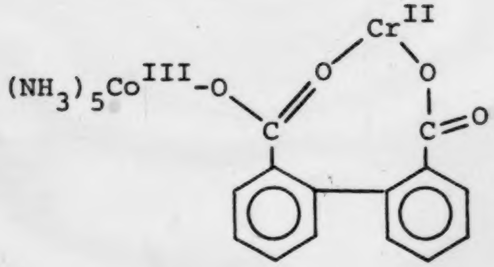
It may be that other complexes thought to proceed by bridged-inner-sphere electron transfer may actually be undergoing reduction by a bridged-outer-sphere mechanism. For example, the nicotinamide complex of $(NH_3)_5Co^{3+}$ [24] was found to give 70% ligand-transfer product and could be using a bridged-outer-sphere intermediate such as VI-1.



VI-1

Conjugation effects are not readily transmitted through meta positions,[184] and as such, the inner-sphere mechanism previously proposed may not be operative. Bridged-outer-sphere reduction is possible since oxidant and reductant are in close proximity.

Gould and Taube[185] observed that dicarboxylate bridging groups on ligands coordinated to cobalt(III) show an $[H^+]^{-1}$ term in the rate law for chromium(II) reduction only when there is potential for chelation between the remote and adjacent (to cobalt) carboxylates as in VI-2.



VI-2

However, the chromium(III) products have extinction coefficients typical of monodentate carboxylato complexes. The ability to form a chelate with the adjacent carboxylate is tantamount to the ability to bring the remotely attached chromium(II) close to the cobalt(III). Thus, the observations could be explained by a bridged-outer-sphere mechanism without chelation in the transition state.

The bridged-outer-sphere mechanism need not be restricted to the reduction of cobalt(III) complexes. Indeed, the results of the present study suggest that such a mechanism may be operative in the reduction of some organochromium(III) complexes. Both $(H_2O)_5CrCH_2CN^{2+}$ and $(H_2O)_5CrCH(CN)CH_2CN^{2+}$ exhibit unusual reactivity toward chromium(II) when compared to other simple chromium(III) complexes.[85,86,100-102] These complexes contain remote nitrile groups capable of binding chromium(II), thereby facilitating reduction by a bridged-outer-sphere mechanism.

Other complexes lacking suitable binding sites such as $(H_2O)_5CrCH_2Cl^{2+}$ [107] and $(H_2O)_5CrCCl_3^{2+}$, [113] are not readily reduced by chromium(II).

The reaction of chromium(II) with $(NH_3)_5CoNCCH_2I^{3+}$ revealed almost quantitative recovery of the novel complex $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$, IV-2. The same species is formed in the reduction of $(NH_3)_5CoNCCH_2Cl^{3+}$, although much lower yields are obtained because outer-sphere reduction of this complex is competitive with halogen abstraction. There can be little doubt as to the nature of IV-2 on the basis of its elution properties, electronic spectrum and the fact that it reacts with mercury(II) to produce $(NH_3)_5CoNCCH_2Hg(OH_2)^{4+}$. Presumably, IV-2 is formed by reaction of a second equivalent of chromium(II) with the initially formed species $(NH_3)_5CoNCCH_2\cdot^{3+}$, obtained by halogen abstraction with chromium(II). Intramolecular electron transfer within $(NH_3)_5CoNCCH_2\cdot^{3+}$ may not be observed because formation of the unstable carbonium ion $NCCH_2^+$ would not be favourable.[125]

In comparison to the cobalt(III) complex, the reaction of chromium(II) with uncomplexed $NCCH_2I$ yielded only 25% $(H_2O)_5CrCH_2CN^{2+}$, IV-1. Even lower yields of IV-1 are obtained in the reduction of $NCCH_2Cl$ but this can be attributed to the fact that the rate of formation of IV-1 is competitive with its decomposition, which is catalyzed by chromium(II). In any event, the low yield of the organochromium(III) product obtained from $NCCH_2I$ is thought to arise from competing pathways of reduction of the initially formed $NCCH_2\cdot$ radical. In addition to simple outer-sphere reduction, which may or may not be operative, chromium(II) can attack either at the nitrile nitrogen to yield $(H_2O)_5CrNCCH_3{}^{3+}$, which may then decompose to acetonitrile and $Cr(OH_2)_6{}^{3+}$, or the reductant may attack the methylene group to yield IV-1. Attack at the nitrile group seems the simplest explanation for the low yield of IV-1 since, when the nitrile is blocked by coordination to cobalt(III), essentially complete recovery of IV-2 is observed.

The reduction of $(NH_3)_5CoNCCH{=}CHCN^{3+}$ by chromium(II) clearly proceeds by a bridged-inner-sphere mechanism as shown by the detection of a product with properties of a chromium(III) nitrile complex, and by the rapid rate of the reduction reaction. The fumaronitrile complex is reduced about 10^7 times faster than the succinonitrile complex although they differ only in the presence of a $-CH_2CH_2-$ rather than a $-CH{=}CH-$ group. This rate enhancement demonstrates how a conjugated bonding system facilitates electron transfer by an inner-sphere mechanism. Since fumaronitrile is readily reducible,[149] it is probable that reduction of the complex occurs by a chemical mechanism.

The results of the kinetic studies on the reaction of chromium(II) with free fumaronitrile are in some doubt, owing to an apparent wavelength dependence of the rate law. This is thought to arise from the formation of an absorbing intermediate which adversely affects the spectrophotometric rate law determination. Evidence for such a species in the free fumaronitrile system was detected in the 360 nm region. Nevertheless, quenching studies and kinetic studies at 750 nm yielded a simple third-order rate law (equation (5.17)) exhibiting a second-order dependence on the reductant concentration. This implies that a second chromium(II) attacks a chromium-fumaronitrile precursor complex, which may be either a radical anion of type $\{Cr^{III}(NCCHCHCN)^{\bar{\cdot}}\}$ or a chromium(II) nitrile complex.

The complicated kinetic results for the reaction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$, V-1, with chromium(II) also might arise from the formation of an absorbing intermediate. Quenching studies were impossible owing to the rapidity of the reaction, and studies at 750 nm proved to be inconclusive. The rate law obtained at 520 nm has been rationalized on the basis of scheme (5.37). However, a satisfactory formulation of "X" in scheme (5.37) has not been found, and the observation of a wavelength dependence on k_{obsd}^{corr} suggests that the proposed mechanism is not operative. The formation of an absorbing intermediate provides the simplest explanation for the results. Nevertheless, it is clear that the reaction is predominantly second-order in chromium(II) and reduction of either $\{\mathrm{Cr^{III}(NCCHCHCN)^{\overset{-}{\cdot}}\text{-}Cr^{III}}\}$ or $\{\mathrm{Cr^{III}(NCCH{=}CHCN)Cr^{II}}\}$ occurs by a reaction with a second equivalent of chromium(II).

The reactions of free fumaronitrile and V-1 with chromium(II) are similar in a number of respects. Both reactions proceed primarily by second-order chromium(II) dependent paths, and both yield a variety of new organochromium(III) complexes. The principal products initially formed in the reduction of free fumaronitrile and V-1 are also similar (V-4 and V-9, respectively) in that each contain two additional equivalents of chromium(III) when compared to their unreduced analogues. The first $(H_2O)_5Cr^{3+}$ is bonded through carbon, while the other is coordinated through a nitrile nitrogen. The other products isolated are of low yields and most appear to arise from decomposition of the principal products, either by aquation or hydrolysis of the nitrile coordinated to $(H_2O)_5Cr^{3+}$. As noted earlier, aquation of the nitrile-bound chromium(III) is much slower than for complexes such as $(H_2O)_5CrNCCH{=}CHCN^{3+}$ and $(H_2O)_5CrNCC_6H_4CN^{3+}$ but similar to that observed for $(H_2O)_5CrNCCH_3{}^{3+}$, thereby suggesting that the nature of the organic ligand plays an important role in determining the kinetic stability of the complex. In addition, both free fumaronitrile and V-1 yield highly-charged species whose nature is uncertain but for which a tentative assignment has been given (Schemes (5.27) and (5.28)).

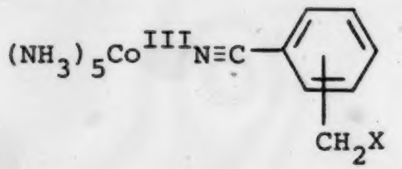
Suggestions for Future Work

As noted earlier, a mechanistic aspect which appears in several sections of this thesis is the bridged-outer-sphere mechanism. Such a mechanism was demonstrated in the chromium(II) reduction of $(NH_3)_5CoNCCH_2CO_2^{2+}$ and was inferred for the malononitrile complex, owing to its greater than expected rate of reduction. Indeed, an awareness of the bridged-outer-sphere mechanism has been important in rationalizing the reactivities toward chromium(II) of the organochromium(III) complexes $(H_2O)_5CrCH_2CN^{2+}$ and $(H_2O)_5CrCH(CN)CH_2CN^{2+}$.

Clearly, a more systematic study of the kinetic features of the bridged-outer-sphere mechanism would be valuable. Different activation parameters might be expected for this mechanism as compared to the non-bridged-outer-sphere case, but the only indication of this to date are the cyanoacetate results reported here. In addition, it is probable that the ligand chain length is an important kinetic feature. Therefore, it would be worthwhile to study the reductions of systems such as

$(NH_3)_5Co^{III}NC(CH_2)_nCO_2^-$.

Information on the importance of the structure of the bridged-outer-sphere intermediate could also be gained from studies on



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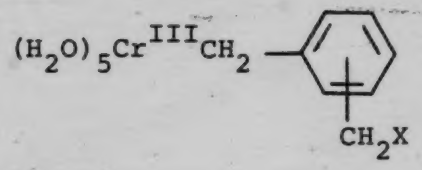
Variation of the position of the CH_2X substituent and the nature of X could provide more information on the features which are important for the bridged-outer-sphere mechanism.

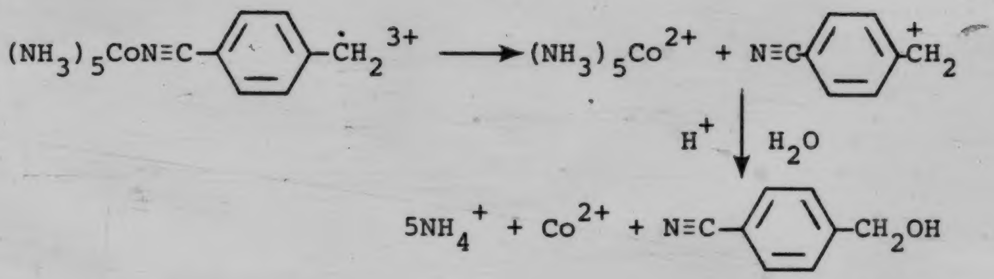
The bridged-outer-sphere mechanism can only be studied for systems in which the group attached to cobalt(III) does not provide a site for adjacent attack. Nitrile, pyridine and amine ligands would seem to be the best candidates for this. These types of complexes can be prepared conveniently by reaction with $[(NH_3)_5CoO_3SCF_3]$-$(CF_3SO_3)_2$ as described in this thesis.

Similar studies on reductions of organochromium(III) complexes would be of value, but the preparation and characterization of appropriate models is much more difficult. Certainly, the chromium(II) reduction of $(H_2O)_5CrCH_2CO_2H^{2+}$ should be studied in more detail than was attempted by Sevcik et al.[111] The bridged-outer-sphere mechanism would predict an $[H^+]^{-1}$ dependence of the rate and formation of $(H_2O)_5CrO_2CCH_3^{2+}$ product. Benzyl complexes of the type



could also be studied in principle. However, it must be noted that benzylchromium(III) complexes undergo Cr-C bond homolysis and are actually stabilized to decomposition by the addition of chromium(II).[35,180] Nevertheless, it is possible that incorporation of suitable functional groups on the ligand may facilitate reduction of the organochromium(III) moiety by a bridged-outer-sphere mechanism.

It was proposed here that $(NH_3)_5CoN{\equiv}CCH_2\cdot^{3+}$ does not undergo intramolecular electron transfer because production of $N{\equiv}C\text{-}CH_2^+$ is thermodynamically unfavourable. To test this proposal and to learn more about intramolecular electron transfer, it would be interesting to generate an analogous, but more oxidizable coordinated radical. A possible system for study is the $(NH_3)_5CoNCC_6H_4CH_2I^{3+}$ - Cr^{2+} system. The radical generated by halogen abstraction could react as follows:



(6.1)

Conjugation would help to stabilize the carbonium ion and might overcome the destabilizing effect of the nitrile function. Even the latter factor could be removed by studying the analogous substituted pyridine system. On the other hand, the study of less easily oxidized radical systems provides a route to novel cobalt(III)-organochromium(III) bimetallic species analogous to complex IV-2.

Finally, reduction of other olefins besides fumaronitrile might be examined. Certainly, a number of olefins have been investigated,[36,37,144-147] but for many of these the kinetic and product studies are at best incomplete. A complete study on free and coordinated (to $(H_2O)_5Cr^{3+}$) olefins may provide additional information about the detailed mechanism of reduction of multiple bonds by chromium(II), as well as by other reductants. Such an investigation may also result in the formation of novel organochromium(III) complexes analogous to those observed for the fumaronitrile systems studied here.

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APPENDIX A

Treatment of Data for Consecutive First-Order Reactions.

a) Consider the consecutive reaction scheme

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \qquad \text{(A-1)}$$

governed by the first-order rate constants k_1, k_2 and k_3. The differential rate equations are

$$\frac{-d[A]}{dt} = k_1[A] \qquad \text{(A-2)}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad \text{(A-3)}$$

$$\frac{d[C]}{dt} = k_2[B] - k_3[C] \qquad \text{(A-4)}$$

$$\frac{d[D]}{dt} = k_3[C] \qquad \text{(A-5)}$$

Integrating these equations and assuming $[A] = [A]_o$, $[B] = [C] = [D] = 0$ at $t = 0$, the following expressions for the concentrations of A, B, C and D at any time t are obtained in terms of $[A]_o$:[1]

$$[A] = [A]_o \exp(-k_1 t) \qquad \text{(A-6)}$$

$$[B] = \frac{[A]_o k_1}{(k_2-k_1)} \{\exp(-k_1 t) - \exp(-k_2 t)\} \qquad \text{(A-7)}$$

$$[C] = [A]_o k_1 k_2 \left\{ \frac{\exp(-k_1 t)}{(k_2-k_1)(k_3-k_1)} + \frac{\exp(-k_2 t)}{(k_1-k_2)(k_3-k_2)} + \frac{\exp(-k_3 t)}{(k_1-k_3)(k_2-k_3)} \right\} \tag{A-8}$$

$$[D] = [A]_o \left\{ 1 - \frac{k_2 k_3 \exp(-k_1 t)}{(k_2-k_1)(k_3-k_1)} - \frac{k_1 k_3 \exp(-k_2 t)}{(k_1-k_2)(k_3-k_2)} - \frac{k_1 k_2 \exp(-k_3 t)}{(k_1-k_3)(k_2-k_3)} \right\} \tag{A-9}$$

The absorbance $A_{\lambda,t}$ at wavelength λ at any time t of a reacting solution in a cell of unit length is given by the expression

$$A_{\lambda,t} = \varepsilon_a[A] + \varepsilon_b[B] + \varepsilon_c[C] + \varepsilon_d[D] \tag{A-10}$$

where ε_a, ε_b, ε_c and ε_d represent the molar extinction coefficients of A, B, C and D, respectively. By substituting equations (A-6) through (A-9) into (A-10) and rearranging terms, on obtains the expression

$$A_{\lambda,t} = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t) + a_3 \exp(-k_3 t) + a_4 \tag{A-11}$$

where

$$a_1 = \varepsilon_a[A]_o + \frac{1}{(k_2-k_1)} \left\{ k_1 \varepsilon_b [A]_o + \frac{k_1 k_2 \varepsilon_c [A]_o - k_2 k_3 \varepsilon_d [A]_o}{(k_3-k_1)} \right\} \tag{A-12}$$

$$a_2 = \frac{k_1}{(k_1-k_2)}\left\{\varepsilon_b[A]_o + \frac{k_2\varepsilon_c[A]_o - k_3\varepsilon_d[A]_o}{(k_3-k_2)}\right\} \tag{A-13}$$

$$a_3 = \frac{k_1k_2}{(k_1-k_3)(k_2-k_3)}\left\{\varepsilon_c[A]_o - \varepsilon_d[A]_o\right\} \tag{A-14}$$

$$a_4 = \varepsilon_d[A]_o \tag{A-15}$$

With $A_{\lambda,t}$, t and $[A]_o$ treated as knowns, non-linear least squares analysis of the data to equation (A-11) yields best fit values for k_1, k_2, k_3, ε_a, ε_b, ε_c and ε_d.

b) Consider the consecutive reaction scheme

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{A-16}$$

Employing the same procedure as shown above, the appropriate rate expression can be derived.[2] Alternatively, the same rate equation can be obtained from equation (A-11) if it is assumed that $k_3 = \varepsilon_d = 0$. Therefore, one obtains

$$A_{\lambda,t} = a_1\exp(-k_1t) + a_2\exp(-k_2t) + a_3 \tag{A-17}$$

where

$$a_1 = \varepsilon_a[A]_o + \frac{1}{(k_2-k_1)}\left\{k_1\varepsilon_b[A]_o - k_2\varepsilon_c[A]_o\right\} \tag{A-18}$$

$$a_2 = \frac{k_1}{(k_1-k_2)}\left\{\varepsilon_b[A]_o - \varepsilon_c[A]_o\right\} \tag{A-19}$$

$$a_3 = \varepsilon_c[A]_o \qquad (A-20)$$

With $A_{\lambda,t}$, t and $[A]_o$ treated as knowns, non-linear least-squares fitting of the data to equation (A-17) yield values for k_1, k_2, ε_a, ε_b and ε_c.

Treatment of Data for Concurrent First-Order Reactions

Consider the situation in which a mixture of species A and B undergo parallel first-order reactions according to the scheme

$$A \xrightarrow{k_1} C \qquad (A-21)$$

$$B \xrightarrow{k_2} D \qquad (A-22)$$

The differential rate equations are

$$-\frac{d[A]}{dt} = \frac{d[C]}{dt} = k_1[A] \qquad (A-23)$$

$$-\frac{d[B]}{dt} = \frac{d[D]}{dt} = k_2[B] \qquad (A-24)$$

Integrating these equations and assuming $[A] = [A]_o$, $[B] = [B]_o$ and $[C] = [D] = 0$ at $t = 0$, the following expressions are obtained:

$$[A] = [A]_o\exp(-k_1t) \qquad (A-25)$$

$$[B] = [B]_o\exp(-k_2t) \qquad (A-26)$$

$$[C] = [A]_o(1-\exp(-k_1t)) \tag{A-27}$$

$$[D] = [B]_o(1-\exp(-k_2t)) \tag{A-28}$$

The absorbance $A_{\lambda,t}$ at wavelength λ at any time t of a reacting solution in a cell of unit length is given by the expression

$$A_{\lambda,t} = \varepsilon_a[A] + \varepsilon_b[B] + \varepsilon_c[C] + \varepsilon_d[D] \tag{A-29}$$

where the various terms are defined as for equation (A-10). By substituting equations (A-25) through (A-28) into (A-29) and rearranging terms, one obtains the expression

$$A_{\lambda,t} = \varepsilon_c[A]_o + \varepsilon_d[B]_o + [A]_o(\varepsilon_a-\varepsilon_c)\exp(-k_1t) + [B]_o(\varepsilon_b-\varepsilon_d)\exp(-k_2t) \tag{A-30}$$

Treating $A_{\lambda,t}$ and t as knowns, non-linear least-squares analysis of the data to equation (A-30) yields best fit values for k_1, k_2, $\varepsilon_c[A]_o + \varepsilon_d[B]_o$, $[A]_o(\varepsilon_a-\varepsilon_c)$, and $[B]_o(\varepsilon_b-\varepsilon_d)$.

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APPENDIX B

APPENDIX B

Spectrophotometric Determination of Acid Dissociation Constants

For reactions of the type

$$RH^{+} \rightleftharpoons R + H^{+} \qquad \text{(B-1)}$$

the equilibrium constant K_a is defined by

$$K_a = \frac{[R][H^{+}]}{[RH^{+}]} \qquad \text{(B-2)}$$

From a consideration of the stoichiometry, it is obvious that

$$C_T = [RH^{+}] + [R] \qquad \text{(B-3)}$$

where C_T is the total complex concentration. Substituting for $[RH^{+}]$ from (B-3) into (B-2) and rearranging gives

$$[R] = \frac{K_a C_T}{K_a + [H^{+}]} \qquad \text{(B-4)}$$

According to Beer's law, the absorbance of a solution is given by

$$A = \ell\varepsilon_{obsd}C_T = \ell\varepsilon_{RH}[RH^{+}] + \ell\varepsilon_R[R] \qquad \text{(B-5)}$$

where ε_{obsd} is the molar extinction coefficient of the given solution as defined by (B-5), ε_{RH} and ε_R are the molar extinction coefficients of the protonated and unprotonated forms of R, respectively, and ℓ is the optical path length in cm. Substituting (B-3) into (B-5) one obtains

$$\ell\varepsilon_{obsd}C_T = \ell\varepsilon_{RH}C_T + \ell(\varepsilon_R-\varepsilon_{RH})[R] \qquad \text{(B-6)}$$

and substituting (B-4) into (B-6) yields

$$\varepsilon_{obsd} = \varepsilon_{RH} + (\varepsilon_R-\varepsilon_{RH})\frac{K_a}{K_a+[H^+]} \qquad \text{(B-7)}$$

From (B-1) it is clear that

$$[H^+] = [H^+]_0 + [R] \qquad \text{(B-8)}$$

where $[H^+]$ is the total acid concentration of the solution which is comprised of both the acid initially added to the solution, $[H^+]_0$, and any acid arising from deprotonation of RH^+. Substituting (B-4) into (B-8) one obtains

$$[H^+] = [H^+]_0 + \frac{K_aC_T}{K_a + [H^+]} \qquad \text{(B-9)}$$

Rearranging (B-9) yields

$$[H^+]^2 + (K_a - [H^+]_0)[H^+] - ([H^+]_0 + C_T)K_a = 0 \qquad \text{(B-10)}$$

After solving the quadratic equation (B-10) for $[H^+]$ as a function of K_a, $[H^+]_0$ and C_T, one obtains

$$[H^+] = \frac{[\{(K_a-[H^+]_0)^2 + 4([H^+]_0 + C_T)K_a\}^{\frac{1}{2}} - (K_a-[H^+]_0)]}{2} \qquad \text{(B-11)}$$

Substituting (B-11) into (B-7) yields

$$\varepsilon_{obsd} = \varepsilon_{RH} + \frac{2(\varepsilon_R - \varepsilon_{RH})K_a}{2K_a + [\{(K_a-[H^+]_0)^2 + 4([H^+]_0 + C_T)K_a\}^{\frac{1}{2}}-(K_a-[H^+]_0)]} \tag{B-12}$$

Knowing ε_{obsd}, $[H^+]_0$ and C_T, non-linear least-squares fitting of the data to equation (B-12) yields the values of K_a, ε_{RH} and ε_R.

APPENDIX C

Table C-1

Equilibrium Data for the Spectrophotometric Determination of the Dissociation Constant of $(NH_3)_5CoNCCH_2CO_2H^{3+}$ [a,b]

Temp., °C	$[H^+]_o$[c], M	ε_{obsd}[d], M^{-1} cm^{-1}	ε_{calc}[e], M^{-1} cm^{-1}
14.6[f]	0.495	41.3	40.5
	0.350	42.1	42.3
	0.199	45.9	46.8
	0.0996	55.1	55.3
	0.0807	58.2	58.6
	0.0601	64.1	63.6
	0.0498	67.9	67.0
	0.0395	71.3	71.4
	0.0292	76.3	77.2
	0.0200	85.4	84.2
	0.0100	96.0	95.0
	0.0075	98.8	98.4
	0.0050	101.2	102.3
	0.0025	105.6	106.7
	0.0	112.2	111.7
25.0[f]	0.495	43.0	43.4
	0.301	47.2	46.9
	0.199	51.5	51.1
	0.0996	61.4	61.2
	0.0807	65.1	65.0
	0.0601	70.4	70.9
	0.0498	75.0	74.9
	0.0395	81.1	80.0
	0.0292	85.8	86.7
	0.0200	94.0	94.6
	0.0100	106.8	106.8
	0.0075	110.6	110.7
	0.0050	114.9	115.0
	0.0025	119.7	119.8
	0.0	126.2	125.3
25.0[g]	3.680	38.9[h]	38.6
	0.485	42.7	44.1
	0.202	51.0	51.7
	0.103	61.0	61.3

	0.0801	67.4	65.9
	0.0601	71.1	71.5
	0.0500	75.5	75.3
	0.0399	80.0	80.0
	0.0301	85.4	85.8
	0.0200	92.8	93.8
	0.0101	104.1	104.5
	0.0075	107.6	108.0
	0.0049	111.9	111.9
	0.0026	116.0	115.7
	0.0	121.2	120.5
35.0[f]	0.495	59.2	59.0
	0.350	61.7	61.5
	0.199	66.7	67.1
	0.0996	77.6	77.9
	0.0807	81.4	82.0
	0.0601	88.1	88.3
	0.0395	98.5	98.0
	0.0292	107.1	105.1
	0.0200	112.9	113.8
	0.0100	126.5	127.0
	0.0750	130.0	131.2
	0.0500	137.2	135.9
	0.0250	141.6	141.2
	0.0	146.8	147.2

---

[a] Ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Determined at 260 nm.

[c] Concentration of acid added to the solution.

[d] Based on total complex concentration in a 5 cm cell.

[e] Calculated by non-linear least-squares fitting of the data to equation (B-12) of Appendix B.

[f] Total complex concentration was 7.67×10^{-4} M.

[g] Total complex concentration was 2.39×10^{-3} M.

[h] Value at $\mu = 3.68$ M ($HClO_4$).

Table C-2

Kinetic Data for the Chromium(II) Reduction of Pentaamminecobalt(III) Complexes of Acetonitrile, Succinonitrile, Cyanoacetamide and Methylcyanoacetate.[a,b]

Ligand	Temperature, °C	10^3x[Co(III)], M	10^2x[Cr(II)], M	[H^+], M	10^2xk, M^{-1} s^{-1}
$NCCH_3$	25.0	6.02	7.36	0.100	0.908
		2.34	5.45	0.216	0.949
		2.34	5.45	0.101	0.938
		2.34	5.45	0.040	0.971
		2.36	3.82	0.100	0.947
	35.0	5.96	7.32	0.100	1.71
		2.32	5.38	0.216	1.71
		2.32	5.38	0.040	1.79
		2.32	3.80	0.101	1.72
	45.0	5.83	7.32	0.101	2.94
		2.40	5.38	0.217	3.10
		2.40	5.38	0.040	3.02
		2.40	3.16	0.102	3.10
$NCCH_2CH_2CN$	25.0	2.23	6.37	0.100	2.47
		1.12	6.37	0.100	2.48
		2.23	4.78	0.100	2.50
		1.12	3.18	0.329	2.61
		1.12	3.18	0.100	2.60
		1.12	3.18	0.041	2.56
	35.1	2.21	6.37	0.100	4.19
		1.11	3.18	0.329	4.38
		2.21	3.18	0.100	4.29
		1.11	3.18	0.100	4.45
		1.11	3.18	0.041	4.45
	45.9	1.11	3.18	0.329	7.75
		2.21	3.18	0.100	7.46
		1.11	3.18	0.100	7.78
		1.11	3.18	0.041	7.73
		1.11	1.59	0.100	7.89
$NCCH_2C(O)NH_2$	25.0	3.20	6.02	0.101	2.52
		1.23	4.09	0.101	2.67
		3.15	4.06	0.101	2.61
		3.08	3.99	0.284	2.59
		3.20	3.99	0.040	2.57

		1.23	2.02	0.101	2.70
	35.0	5.71	7.32	0.101	4.12
		2.35	5.38	0.217	4.13
		2.35	5.38	0.040	4.36
		2.35	3.16	0.102	4.39
	45.3	3.14	4.03	0.103	7.17
		1.35	3.05	0.102	7.45
		1.35	2.03	0.390	7.38
		1.35	2.03	0.040	7.59
$NCCH_2CO_2CH_3$	25.0	3.09	6.02	0.100	2.28
		1.20	4.10	0.101	2.40
		3.19	3.99	0.285	2.33
		3.09	3.99	0.100	2.27
		3.09	3.99	0.040	2.36
	35.0	5.52	7.32	0.101	3.93
		2.27	5.38	0.217	4.02
		2.27	5.38	0.040	4.18
		2.27	3.16	0.102	4.14
	45.4	3.16	4.03	0.103	6.88
		1.35	3.05	0.102	6.82
		1.35	2.03	0.390	6.97
		1.35	2.03	0.040	7.17

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[a]For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b]Determined at 467 nm.

Table C-3

Kinetic Data for the Reduction of $(NH_3)_5CoNCCH_2CO_2H^{3+}$ by Chromium(II).[a]

Temp., °C	10^3x[Co(III)], M	10^3x[Cr(II)], M	[H^+], M	k_{obsd},[b] M^{-1} s^{-1}	k_{calc},[c] M^{-1} s^{-1}
14.9	0.82	1.01	0.445	0.0682	0.0698
	1.42	2.01	0.375	0.0799	0.0796
	1.42	3.02	0.301	0.0972	0.0945
	1.42	2.02	0.301	0.0953	0.0945
	2.53	3.04	0.241	0.117	0.112
	1.42	3.04	0.240	0.116	0.113
	1.42	2.02	0.240	0.114	0.113
	1.42	2.02	0.201	0.128	0.130
	1.42	3.04	0.201	0.133	0.130
	1.42	2.02	0.141	0.170	0.171
	1.42	2.02	0.100	0.215	0.221
	0.80	2.02	0.075	0.255	0.271
	0.80	2.02	0.050	0.348	0.352
	0.80	1.01	0.040	0.384	0.400
	0.48	1.01	0.030	0.473	0.465
25.0	0.84	1.01	0.445	0.147	0.143
	1.43	2.02	0.375	0.167	0.164
	1.43	2.02	0.300	0.200	0.196
	1.69	3.01	0.299	0.199	0.195
	1.43	2.02	0.240	0.236	0.234
	2.00	2.13	0.200	0.277	0.271
	0.84	1.01	0.201	0.279	0.270
	1.69	2.03	0.140	0.357	0.358
	0.81	1.78	0.142	0.366	0.356
	2.03	4.25	0.102	0.465	0.460
	1.69	2.03	0.101	0.456	0.461
	1.02	1.42	0.100	0.465	0.462
	2.00	2.13	0.074	0.572	0.574
	0.85	1.01	0.075	0.553	0.570
	2.00	2.13	0.050	0.741	0.745
	0.84	1.01	0.050	0.739	0.745
	0.80	2.20	0.040	0.882	0.850
	0.42	1.01	0.040	0.881	0.850
	0.81	1.76	0.030	1.03	0.992
	0.42	1.01	0.030	1.03	0.992
35.1	0.85	1.01	0.445	0.289	0.277
	0.85	1.01	0.374	0.331	0.319

0.85	1.01	0.301	0.394	0.380
0.85	1.01	0.240	0.460	0.458
0.85	1.01	0.200	0.515	0.531
0.85	1.01	0.142	0.675	0.699
0.85	1.01	0.100	0.859	0.916
0.82	1.01	0.074	1.07	1.14
0.42	0.50	0.074	1.06	1.14
0.42	1.00	0.050	1.47	1.48
0.42	0.50	0.050	1.42	1.48
0.42	0.50	0.040	1.74	1.70
0.42	0.50	0.030	2.03	1.99

---

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Determined at 467 nm.

[c] Values for k_{calc} were obtained by simultaneously fitting all the data of three temperatures to the transition-state equation using the activation parameters obtained from the methylcyanoacetate reduction for the k_1 pathway.

Table C-4

Kinetic Data for Reduction of $(NH_3)_5CoNCCH_2CN^{3+}$ by by Chromium(II) at 25.0°[a]

10^3x[Co(III)], M	10^2x[Cr(II)], M	$[H^+]$ M	10^2xk_1',[b] M^{-1} s^{-1}	10^2xk_2',[b] M^{-1} s^{-1}
1.62	2.01	0.393	6.68	1.11
1.48	2.01	0.200	7.05	1.11
2.06	5.99	0.198	6.80	0.94
1.64	2.01	0.100	7.86	1.20
1.62	2.01	0.070	8.26	0.86
1.63	2.01	0.050	9.33	1.21
1.63	2.99	0.039	9.65	0.86
1.60	2.01	0.039	9.74	0.90
2.05	5.99	0.039	10.1	0.88

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$) and λ = 467 nm.

[b] Values of k_1' and k_2' were obtained from least-squares fitting of absorbance data to the reaction scheme $A \xrightarrow{k_1'} C$ and $B \xrightarrow{k_2'} D$ as described in Appendix A.

Table C-5

Kinetic Data for the Reaction of $NCCH_2I$ with Chromium(II)[a]

Temp., °C	10^3x[$NCCH_2I$], M	10^2x[Cr(II)], M	[H^+], M	k,[b] M^{-1} s^{-1}
15.3	2.5	5.13	0.249	6.83
	2.5	5.13	0.051	6.97
	1.2	2.57	0.249	6.53
	1.2	2.57	0.051	6.69
25.0	2.5	5.13	0.249	9.31
	2.5	5.13	0.050	9.73
	1.2	2.57	0.249	9.01
	1.2	2.57	0.100	8.92
	0.92	1.28	0.100	8.97
35.0	2.5	5.13	0.249	13.4
	2.5	5.13	0.051	14.0
	1.2	2.57	0.249	12.5
	1.2	2.57	0.051	13.2

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[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Determined at 528 nm.

Table C-6

Kinetic Data for Reaction of $NCCH_2Cl$ with Chromium(II) at 25°C[a]

$10^3 \times [NCCH_2Cl]$, M	$10^2 \times [Cr(II)]$, M	$[H^+]$, M	$10^2 \times k_1$,[b,c] $M^{-1}s^{-1}$
2.8	7.00	0.160	1.05
2.8	7.01	0.080	1.04
2.8	7.01	0.025	1.09
1.5	3.50	0.329	1.02
1.5	3.51	0.080	1.17

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Determined at 609 nm.

[c] Values of k_1 were obtained from non-linear least-squares fitting of absorbance data to the reaction scheme $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, where k_2 was held constant at the value for Cr^{2+} catalyzed aquation of $(H_2O)_5CrCl^{2+}$.

Table C-7

Kinetic Data for Reaction of $(H_2O)_5CrCH_2CN^{2+}$ with Chromium(II) at 25°C.[a]

10^3x[Cr(III)], M	10^2x[Cr(II)], M	$[H^+]$, M	10^2xk_{obsd},[b] M^{-1} s^{-1}	10^2xk_{calc},[c] M^{-1} s^{-1}
0.56	2.17	0.393	1.86	1.87
1.12	4.34	0.286	1.88	1.93
1.12	1.08	0.286	1.95	1.93
0.56	2.17	0.149	2.14	2.11
0.56	2.17	0.100	2.33	2.29
1.12	2.17	0.070	2.52	2.53
1.12	4.34	0.050	2.80	2.85
1.12	2.17	0.050	2.88	2.85

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Determined at 409 nm.

[c] Calculated from the equation $k_{obsd} = k_1 + k_2K_a/[H^+]$, where $k_1 = 1.73 \times 10^{-2}$ M^{-1} s^{-1} and $k_2K_a = 5.62 \times 10^{-4}$ s^{-1}.

Table C-8

Kinetic Data for Reaction of $(H_2O)_5CrCH_2CN^{2+}$ with Mercury(II) at 25.0°.[a]

10^4x[Cr(III)], M	10^2x[Hg(II)], M	$[H^+]$, M	k,[b] M^{-1} s^{-1}
6.0	0.0600	0.504	8.46
6.0	0.0200	0.501	8.01
6.0	0.0600	0.040	8.25
3.0	0.0200	0.040	9.03

[a] For all runs, ionic strength 1.00 M ($LiClO_4$-$HClO_4$).

[b] Determined at 409 nm.

Table C-9

Kinetic Data for Reaction of $(NH_3)_5CoNCCH_2I^{3+}$ with Chromium(II).[a]

Temp., °C	10^3x[Co(III)], M	10^2x[Cr(II)], M	$[H^+]$, M	k,[b,c] M^{-1} s^{-1}
15.3	1.18	5.13	0.244	35.9
	1.15	5.13	0.051	36.8
	1.16	2.57	0.244	36.4
	1.16	2.57	0.051	37.9
25.0	1.16	3.00	0.348	43.8(43.7)
	1.15	3.00	0.100	46.2(46.2)
	1.17	3.00	0.049	46.4
	1.15	5.03	0.100	46.3(46.0)
	0.56	1.02	0.247	43.9
35.4	1.16	5.13	0.244	59.9
	1.17	5.13	0.051	61.2
	1.17	2.57	0.244	60.1
	1.17	2.57	0.100	60.9

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Determined at 477 nm unless otherwise noted.

[c] Values in parentheses were determined at 650 nm.

Table C-10

Kinetic Data for Reaction of $(NH_3)_5CoNCCH_2Cl^{3+}$ with Chromium(II) at 25°C.[a]

10^3x[Co(III)], M	10^2x[Cr(II)], M	$[H^+]$, M	10^2xk_1, M^{-1} s^{-1}
1.23	4.33	0.100	9.4[b]
1.23	2.16	0.387	8.9[b]
1.21	4.33	0.100	9.9[c]
1.20	4.33	0.050	9.5[c]
1.19	2.16	0.387	9.7[c]
2.22	6.53	0.102	7.6[c]
1.23	4.33	0.387	8.3[c]

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Reaction was monitored at 609 nm. Values of k_1 were obtained from least-squares fitting of absorbance data to the scheme $A \xrightarrow{k_1} B \xrightarrow{k_2} C$.

[c] Reaction was monitored at 417 nm. Values of k_1 were obtained from least-squares fitting of absorbance data to the scheme $A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$.

Table C-11

Kinetic Data for the Chromium(II) Reduction of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ at 25.0°C.[a]

10^3x[Co(III)], M	10^2x[Cr(II)], M	$[H^+]$, M	10^3xk,[b] $M^{-1}\ s^{-1}$
0.95	6.49	0.170	2.42
1.90	6.49	0.049	2.44
1.90	6.49	0.156	2.26
1.90	3.25	0.312	2.39[c]
1.90	3.25	0.049	2.47

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Determined at 477 nm unless otherwise noted.

[c] Determined at 417 nm.

Table C-12

Kinetic Data for Reaction of $(NH_3)_5CoNCCH_2Cr(OH_2)_5^{5+}$ with Mercury(II) at 25°C[a]

$10^3 \times [Co(III)]$, M	$10^2 \times [Hg(II)]$, M	$[H^+]$, M	$10^2 \times k_{obsd}$,[b] $M^{-1}\ s^{-1}$	$10^2 \times k_{calc}$,[c] $M^{-1}\ s^{-1}$
0.37	1.63	0.946	3.42	3.55
1.11	3.27	0.738	3.53	3.57
0.37	3.27	0.287	3.87	3.69
1.11	8.17	0.171	3.77	3.83
0.37	1.63	0.170	4.03	3.83
0.37	3.27	0.080	4.34	4.21
0.37	3.27	0.053	4.57	4.58
0.37	1.63	0.052	4.60	4.60

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[a] For all runs, ionic strength 1.00 M ($LiClO_4$-$HClO_4$).

[b] Determined at 417 nm.

[c] Calculated from the equation $k_{obsd} = k_1 + k_2K_a/[H^+]$, with $k_1 = 3.49 \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k_2K_a = 5.8 \times 10^{-4}\ s^{-1}$.

Table C-13

Kinetic Data for the Chromium(II) Reduction of $(NH_3)_5CoNCCH{=}CHCN^{3+}$ at 25°[a,b]

$10^4 x [Co(III)]$, M	$10^4 x [Cr(II)]$, M	$[H^+]$, M	$10^{-5} x k$,[c] $M^{-1} s^{-1}$
0.30	3.1	0.100	2.0[d]
0.15	2.3	0.100	1.9[d]
0.15	1.5	0.250	1.8[d]
0.15	1.5	0.100	2.0[d]
0.15	1.5	0.050	2.0[d]
0.73	3.4	0.250	2.1
1.46	3.4	0.025	2.2
0.73	1.7	0.250	1.7
0.73	1.7	0.100	1.6
0.73	1.7	0.025	1.6
0.62	1.5	0.100	1.9
0.31	1.5	0.100	1.9
0.73	1.0	0.100	1.6
0.37	1.0	0.026	1.6

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Wavelength 260 nm.

[c] Unless otherwise noted, data obtained under second-order conditions using equation (2.1).

[d] Pseudo-first-order conditions.

Table C-14

Kinetic Data for Aquation of $(H_2O)_5CrNCCH{=}CHCN^{3+}$ at 25°C[a,b]

10^3x[Co(III)],[c] M	10^3x[Cr(II)], M	[H^+], M	10^2xk_{obsd}, s^{-1}	10^2xk_{calc},[d] s^{-1}
3.73	3.58	0.442	1.27	1.28
3.72	3.58	0.251	1.36	1.35
0.91	0.87	0.240	1.34	1.36
3.72	3.58	0.101	1.66	1.60
3.73	3.58	0.051	1.97	2.00
3.74	1.87	0.049	2.00	2.03
3.73	3.58	0.034	2.44	2.41
3.73	3.58	0.026	2.84	2.78
3.74	1.87	0.025	2.78	2.84

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Wavelength 395 nm.

[c] $(H_2O)_5CrNCCH{=}CHCN^{3+}$ is formed by reduction of the cobalt(III) fumaronitrile complex.

[d] Calculated from equation $k_{calc} = 1.19 \times 10^{-2} + \frac{4.14 \times 10^{-4}}{[H^+]}$.

Table C-15

Kinetic Data for Reaction of Chromium(II) with $(H_2O)_5CrCH(CN)CH_2CN^{2+}$ at 25°C[a,b]

$10^3 \times [Cr(III)]$, M	$10^2 \times [Cr(II)]$, M	$[H^+]$, M	$10^2 \times k$, $M^{-1}\ s^{-1}$
0.86	1.51	0.050	1.21
1.9	2.48	0.376	1.18
1.9	2.48	0.100	1.22
0.86	2.49	0.020	1.23
1.9	5.04	0.100	1.16
1.9	7.52	0.100	1.15

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Wavelength 411 nm.

Table C-16

Kinetic Data for Aquation of $(H_2O)_5CrCH(CN)CH_2CNCr(OH_2)_5^{5+}$ at 25°C[a,b]

$10^3 \times [V-4]$, M	$[H^+]$, M	$10^4 \times k$, s^{-1}
1.65	0.330	3.65
1.42	0.316	3.54[c]
1.12	0.116	3.56
1.65	0.025	3.70
1.42	0.025	3.55[c]

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Wavelength 510 nm.

[c] Solutions were deoxygenated by purging with argon for 10 minutes.

Table C-17

Kinetic Data for Reaction of Chromium(II) with $(H_2O)_5CrCH(CN)CH_2CNCr(OH_2)_5^{5+}$ at 25°C.[a,b,c]

10^4x[V-4], M	10^2x[Cr(II)], M	$[H^+]$, M	10^4xk_1,[d,f] s^{-1}	10^4xk_1,[e,f] s^{-1}
6.4	6.06	0.142	4.80 ± 0.09	4.71 ± 0.06
6.4	3.03	0.142	4.31 ± 0.11	4.05 ± 0.09
6.4	1.51	0.142	4.75 ± 0.51	3.89 ± 0.23
6.4	1.51	0.364	4.52 ± 0.31	3.77 ± 0.12

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Wavelength 408 nm.

[c] Data fitted to reaction scheme $A \xrightarrow{k_1} B \xrightarrow{k_2} C$.

[d] Values of k_1 obtained with k_2 held constant at $1.19 \times 10^{-2}\ M^{-1}\ s^{-1}$.

[e] Values of k_1 obtained with k_2 held constant at $1.25 \times 10^{-2}\ M^{-1}\ s^{-1}$.

[f] Errors quoted are 95% confidence limits.

Table C-18

Kinetic Data For Reduction of NCCH=CHCN by Chromium(II) at 25°C and 520 nm.[a]

10^3x [NCCH=CHCN], M	10^2x [Cr(II)], M	[H^+] M	10^3xk_1,[b] s^{-1}	10^3xk'_1,[c] s^{-1}
1.85	3.23	0.338	2.17	2.20
1.85	3.43	0.338	2.45	2.47
1.85	3.29	0.335	2.19	2.21
1.85	3.23	0.200	2.22	2.23
1.85	3.43	0.200	2.60	2.69
1.85	3.29	0.200	2.33	2.41
2.50	4.87	0.201	5.76	5.74
1.85	3.23	0.100	2.58	2.85
0.93	3.23	0.100	2.64	2.86
0.93	1.62	0.100	0.722	0.937
0.92	1.64	0.100	0.710	0.939
2.50	6.56	0.100	10.9	10.5
2.50	4.95	0.100	6.32	6.71
0.92	2.31	0.100	1.41	1.60
2.50	4.87	0.100	6.76	6.83
1.85	3.23	0.075	2.75	3.14
1.85	3.23	0.050	2.71	3.16
2.50	6.47	0.050	11.0	11.8
1.85	3.29	0.050	2.74	3.21
2.50	6.58	0.050	11.8	12.4
2.50	4.95	0.050	6.47	7.01
0.92	2.31	0.050	1.42	1.82
0.92	3.43	0.025	3.25	3.81
0.92	3.29	0.025	2.86	3.47
0.92	3.23	0.025	2.88	3.46

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[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Values of k_1 were obtained by non-linear least-squares fitting of absorbance data to the scheme $A \xrightarrow{k_1} B \xrightarrow{k_3} C$.

[c] Values of k'_1 were obtained by non-linear least-squares fitting of absorbance data to the scheme $A \xrightarrow{k'_1} B \xrightarrow{k'_2} C \xrightarrow{k'_3} D$ where k'_2 was held constant at the value 3.6 x 10^{-4} s^{-1}, which is the rate constant for aquation of complex V-4.

Table C-19

Kinetic Data for Reduction of NCCH=CHCN by Chromium(II) at 25°C and 750 nm.[a]

10^3x [NCCH=CHCN], M	10^2x [Cr(II)], M	[H^+], M	k, M^{-2} s^{-1}
1.55	2.00	0.400	2.72
2.03	2.99	0.354	3.05
2.03	2.99	0.025	2.83
4.00	5.99	0.209	2.59
4.00	5.99	0.025	2.51

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

Table C-20

Kinetic Data for Absorbance Decrease in Reaction of NCCH=CHCN With Chromium(II) at 25°C and 520 nm.[a]

10^3x [NCCH=CHCN], M	10^2x [Cr(II)], M[b]	[H^+], M	10^3xk_3,[c] M^{-1} s^{-1}	10^2xk_3',[d] M^{-1} s^{-1}
1.85	3.23	0.338	7.43	0.94
1.85	3.43	0.338	7.55	0.89
1.85	3.29	0.335	7.20	0.89
1.85	3.23	0.200	7.62	0.90
1.85	3.43	0.200	7.96	1.04
1.85	3.29	0.200	7.54	0.86
2.50	4.87	0.201	7.08	0.77
1.85	3.23	0.100	7.24	1.23
0.93	3.23	0.100	7.74	1.24
0.93	1.62	0.100	8.70	1.22
0.92	1.64	0.100	9.15	1.22
2.50	6.56	0.100	5.35	1.26
2.50	4.95	0.100	5.86	1.27
0.92	2.31	0.100	8.44	1.14
2.50	4.87	0.100	6.59	0.90
1.85	3.23	0.075	7.59	1.22
1.85	3.23	0.050	6.93	1.22
2.50	6.47	0.050	5.77	0.95
1.85	3.29	0.050	6.87	1.16
2.50	6.58	0.050	5.23	1.28
2.50	4.95	0.050	5.80	1.18
0.92	2.31	0.050	8.48	1.26
0.92	3.43	0.025	7.14	1.43
0.92	3.29	0.025	7.02	1.39
0.92	3.23	0.025	7.18	1.43

Footnotes for Table C-20

[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Values reported are the initial concentrations of reductant. The second-order rate constants (k_3 and k_3') were calculated after correcting for the chromium(II) consumed in the initial phase of the reaction.

[c] Values of k_3 were obtained by non-linear least-squares fitting of absorbance data to the scheme $A \xrightarrow{k_1} B \xrightarrow{k_3} C$.

[d] Values of k_3' were obtained by non-linear least-squares fitting of absorbance data to the scheme $A \xrightarrow{k_1'} B \xrightarrow{k_2'} C \xrightarrow{k_3'} D$ where k_2' was held constant at the value 3.6×10^{-4} s^{-1} which is the rate constant for aquation of V-4.

Table C-21

Kinetic Data for Hydrolysis of Complex V-9 at 25°C.[a]

10^4x [Co(III)],[b] M	10^2x [Cr(II)], M	[H^+], M	k,[c] s^{-1}
20.5	3.00	0.350	0.107[d]
3.91	3.01	0.349	0.0976
4.02	3.01	0.100	0.114
4.02	3.01	0.051	0.110
3.91	3.01	0.025	0.104
20.1	3.00	0.025	0.110[d]
4.04	2.96	0.025	0.0980
3.95	1.94	0.400	0.111
3.95	1.94	0.025	0.0950
3.98	1.47	0.025	0.0901
3.98	1.47	0.010	0.110

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[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Values reported represent the initial concentration of $(NH_3)_5CoNCCH{=}CHCN^{3+}$. Reaction with chromium(II) generates complex V-1 which is subsequently reduced to complex V-9.

[c] Determined at 355 nm unless otherwise noted.

[d] Determined at 750 nm.

Table C-22

Kinetic Data for Reduction of $(H_2O)_5CrNCCH{=}CHCN^{3+}$ by Chromium(II) at 25°C.[a]

10^4x [Co(III)],[b] M	10^2x [Cr^{2+}], M	[H^+], M	k_{obsd},[c] s^{-1}	k^{corr}_{obsd},[f] s^{-1}	k^{corr}_{calc},[g] s^{-1}
2.0	0.48	0.400	0.0540(0.0530)[d]	0.0411	0.0424
2.0	0.48	0.200	0.0587(0.0570)[d]	0.0447	0.0478
2.0	0.48	0.100	0.0688	0.0527	0.0530
2.0	0.48	0.048	0.0823	0.0618	0.0620
2.0	0.48	0.033	0.0971(0.0980)[d]	0.0725	0.0703
4.1	0.95	0.398	0.172	0.159	0.151
4.1	0.95	0.199	0.186(0.172)[d]	0.172	0.170
2.0	0.95	0.098	0.211	0.195	0.187
4.2	0.95	0.048	0.240	0.220	0.209
4.2	0.95	0.038	0.248(0.240)[d]	0.225	0.218
4.1	0.95	0.028	0.257	0.230	0.234
4.2	0.95	0.023	0.273	0.243	0.246
4.0	1.46	0.398	0.357(0.315)[d]	0.344	0.325
4.0	1.46	0.199	0.406	0.392	0.378
4.0	1.46	0.147	0.443	0.428	0.396
4.0	1.46	0.099	0.483	0.467	0.418
4.0	1.46	0.099	0.477	0.461	0.418
3.9	1.46	0.067	0.492	0.474	0.440
4.0	1.46	0.049	0.504	0.484	0.460
3.9	1.46	0.038	0.512(0.503)[d]	0.489	0.477
3.9	1.46	0.028	0.531	0.504	0.503
4.0	1.48	0.025	0.535	0.507	0.522
2.0	1.48	0.024	0.554	0.525	0.533
4.0	1.46	0.023	0.543	0.513	0.524
4.1	1.94	0.400	0.564(0.510)[d]	0.551	0.530
3.9	1.94	0.395	0.575	0.562	0.533
4.0	1.94	0.298	0.625	0.612	0.578
4.1	1.94	0.199	0.674(0.620)[d]	0.660	0.634
3.9	1.94	0.147	0.710	0.695	0.670
4.0	1.94	0.099	0.758	0.742	0.712
4.0	1.94	0.067	0.782	0.764	0.749
4.2	1.94	0.067	0.782	0.764	0.749
3.9	1.94	0.049	0.813	0.793	0.781
4.0	1.94	0.049	0.807(0.805)[d]	0.787	0.781
3.9	1.94	0.039	0.846	0.823	0.805

3.9	1.94	0.028	0.877	0.850	0.845
4.0	1.94	0.025	0.886(0.895)[d]	0.858	0.863
3.9	1.94	0.023	0.897	0.867	0.875
4.0	2.96	0.352	1.13(0.920)[d]	1.12	1.12
6.0	3.01	0.349	1.13(0.951)[d]	1.12	1.16
20.5	3.00	0.350	(0.950)[e]		
4.0	3.01	0.273	1.25(1.05)[d]	1.24	1.26
4.2	2.99	0.200	1.33(1.22)[d]	1.32	1.37
3.9	2.96	0.147	1.40(1.40)[d]	1.38	1.44
2.0	2.99	0.147	1.40	1.38	1.46
3.9	3.01	0.100	1.48	1.46	1.60
4.0	2.96	0.099	1.48	1.46	1.55
2.0	2.96	0.099	1.47	1.45	1.55
4.0	2.96	0.067	1.62	1.60	1.65
4.0	3.01	0.051	1.66(1.64)[d]	1.64	1.77
3.9	2.96	0.048	1.66	1.64	1.73
4.0	2.96	0.038	1.72	1.70	1.78
4.0	2.96	0.028	1.80	1.77	1.85
4.0	2.96	0.025	1.85(1.85)[d]	1.82	1.88
20.1	3.00	0.025	(1.84)[e]		
3.9	2.96	0.023	1.85	1.82	1.90

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[a] For all runs, ionic strength 0.50 M ($LiClO_4$-$HClO_4$).

[b] Values reported are the initial concentrations of $(NH_3)_5CoNCCHCHCN^{3+}$. Reaction with chromium(II) yields complex V-1.

[c] The rate constants were obtained at 520 nm unless otherwise noted.

[d] Determined at 410 nm.

[e] Determined at 750 nm.

[f] Values tabulated have been corrected for the aquation of complex V-1 (equation (5.8)). Only the results obtained at 520 nm are listed.

[g] Values for k^{corr}_{calc} were obtained from equation (5.22) using the values of the parameters given there. Values of k^{calc}_{corr} are listed only for runs at 520 nm.